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STUDY OF THE MECHANISM OF CHEMICAL REACTIVITY  
OF NITROGEN DIOXIDE WITH TRIMETHYLALUMINE

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A STUDY OF THE MECHANISM OF CHEMICAL REACTIVITY  
OF NITROGEN TETROXIDE WITH TITANIUM ALLOYS


FINAL REPORT  
July 1, 1967 through August 30, 1968

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Foreword

This is a final report prepared by the Research Center, Hercules Incorporated, under Contract No. NAS8-21207, Control Number DCN 1-7-54-20173 (1F) for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration, and covering the period from July 1, 1967 through August 30, 1968. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division, of the George C. Marshall Space Flight Center with Mr. W. A. Riehl acting as project manager. Scientific personnel that have participated in this program include:

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### ABSTRACT

The overall purpose of this program was to study the interactions between liquid dinitrogen tetroxide ( $N_2O_4$ ) and 6Al 4V titanium alloy that lead to stress corrosion cracking. The study was almost exclusively focused on establishing the chemical composition of the minor constituents of reactive and nonreactive  $N_2O_4$  systems. The specific objectives of the program were:

(1) To develop a standard stress corrosion test capable of assessing the corrosive nature of various types of dinitrogen tetroxide ( $N_2O_4$ ) on 6Al 4V titanium alloy specimens.

(2) To develop methods of analysis capable of detecting and determining significant differences between various types of  $N_2O_4$ .

(3) To identify that constituent or component of  $N_2O_4$  which enhances or induces stress corrosion in 6Al 4V titanium alloy.

(4) To attempt to establish the possible presence of stress corrosion inhibitors in certain types of  $N_2O_4$  and to determine the concentration levels that are critical regarding their inhibitory action.

The majority of the specific experimental goals of the program were achieved. A satisfactory stress corrosion cracking test was developed and found to give extremely consistent results. Six new analytical methods were developed that are capable of detecting and determining significant difference in the minor constituent composition of different types of  $N_2O_4$ . These include:

- (1) Combined nitric oxide (visible spectrophotometer).
- (2) Total protons (NMR).
- (3) Distribution of protonated species (near-infrared spectroscopy).
- (4) Dissolved oxygen (gas chromatography).
- (5) Combined chlorine (x-ray fluorescence).
- (6) Metallic impurities (atomic absorption).

Methods (1) and (4) permit analyses to be made at previously unattainable low levels. Method (2) represents a major analytical breakthrough. It is now possible to establish the amount and nature of the protonated species in samples of liquid  $N_2O_4$ . Oxygenated  $N_2O_4$  was found to contain only  $HNO_3$ ; nonoxygenated  $N_2O_4$  was found to contain variable amounts of  $HNO_3$ ,  $HNO_2$ , and  $H_2O$ . In addition, techniques were developed for the quantitative adjustment of the minor constituent composition of  $N_2O_4$  systems, including a method for substantially reducing the level of protonated species.

By application of the above techniques and methods it was possible to prepare and test a wide variety of  $N_2O_4$  compositions. As a result, the SCC test behavior of 6Al 4V titanium alloy in the commonly encountered types of commercial  $N_2O_4$  was established. Correlation of combined NO-protonated species concentrations with SCC test behavior was partially achieved in terms of critical concentrations. An interdependency between combined NO and protonated species concentrations was shown to relate to SCC test behavior. An attempt also was made to establish the effect of dissolved  $O_2$  concentration.

It is now believed that the presence of  $\text{HNO}_2$  and/or  $\text{H}_2\text{O}$  species in  $\text{N}_2\text{O}_4$  are the main critical indicators of a nonreactive system that is free of extraneous contamination. However, the nature of the inhibitory process has not been established. The available evidence appears to favor the hypothesis of an oxidative attack mechanism, although the specific nature of the attacking species remains unknown.

Fundamental aspects of the overall problem remain unresolved and some tentative conclusions arrived at during the course of this work require further experimental verification. Suggestions for future work have been made. Detailed procedures for the SCC test and analytical methods are included in this report.

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### INTRODUCTION

In 1965, Bell Aerosystems Company was conducting routine thirty-day storability tests of propellant-grade dinitrogen tetroxide ( $N_2O_4$ ) in 6Al 4V titanium alloy tanks. On July 12, an Apollo service module propellant tank burst 34 hours after start of the test. There had been no previous indication that the two materials were incompatible. The aerospace industry had considered titanium and its alloys to have generally excellent corrosion resistance, and their use with  $N_2O_4$  under a wide variety of environmental and stress conditions was recommended. No other aerospace company that employed 6Al 4V titanium alloy tanks to store  $N_2O_4$  had encountered any problems. Subsequent extensive testing at Bell confirmed that the phenomenon could be reproduced under the same conditions of stress, temperature, and time. Failure analysis indicated that the fundamental problem was stress corrosion cracking caused by a reaction between the stressed titanium alloy and  $N_2O_4$ . The fact that the stress level in the thin-walled Apollo tanks was approximately 90% of yield strength under the test conditions appeared to be one of the reasons that other alloy users operating at substantially lower stress levels had not encountered difficulties. Another possible reason was that various lots of  $N_2O_4$  from the two suppliers (Hercules Incorporated and Allied Chemical Corporation) appeared to differ very significantly in their reactivity with titanium alloys even though all lots met purchase specifications. Even greater confusion arose when



experimental evidence was obtained that showed a definite correlation of the color of the  $\text{N}_2\text{O}_4$  with its reactivity.

Dinitrogen tetroxide exists as an equilibrium mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  over most of the gas-liquid-solid range. At the freezing point ( $-11.2^\circ\text{C}.$ ), the solid is colorless and undissociated but the liquid is yellow due to the presence of about 0.03%  $\text{NO}_2$ . As the temperature is raised, the liquid darkens to reddish-yellow as dissociation increases. At the boiling point ( $21.12^\circ\text{C}.$ ), the liquid contains about 0.13%  $\text{NO}_2$  and the vapor about 16%  $\text{NO}_2$ . Small amounts of  $\text{NO}$  dissolved in  $\text{N}_2\text{O}_4$  react with equilibrium amounts of  $\text{NO}_2$  to form  $\text{N}_2\text{O}_3$ . The presence of  $\text{N}_2\text{O}_3$  imparts a green color to  $\text{N}_2\text{O}_4$ .

It so happened that normal production  $\text{N}_2\text{O}_4$  from the two different manufacturing processes employed by Hercules and Allied contained a small amount of  $\text{N}_2\text{O}_3$  and thus had a greenish hue. Even though the material met specifications, the color was objected to by Bell and other aerospace users. Accordingly, both Hercules and Allied modified their manufacturing processes to include an air oxidation step that converted the  $\text{N}_2\text{O}_3$  to  $\text{N}_2\text{O}_4$  and changed the color from green to reddish yellow. From this point on, stress corrosion cracking problems appeared. All of the tank failures were associated with oxygenated, red  $\text{N}_2\text{O}_4$ ; no tanks failed in tests with green  $\text{N}_2\text{O}_4$ . After substantial additional testing, the aerospace users, with concurrence by the Air Force and NASA, requested a change back to green  $\text{N}_2\text{O}_4$ . Shortly after this decision, NASA officially adopted green  $\text{N}_2\text{O}_4$ .

as the Apollo oxidizer and published a specification (MSC-PPD-2A) that defined green  $N_2O_4$  in terms of the combined NO content.

Although an eminently satisfactory solution to the immediate stress corrosion cracking problem had been achieved, the mechanism of the interaction between  $N_2O_4$  and 6Al 4V titanium alloy remained unknown. The extensive analytical and testing work performed in connection with this problem empirically established a number of general composition-reactivity relationships in the 6Al 4V titanium alloy- $N_2O_4$  system. However, it also clearly established the fact that currently available analytical methods were totally inadequate to establish the critical composition parameters that define reactive and nonreactive  $N_2O_4$ . Recognition of these facts by NASA led to the issuance of a Request for Proposal by the George C. Marshall Space Flight Center in May 1967 and the awarding of a contract to Hercules Incorporated in July 1967. This contract differed from other related studies in that it was almost exclusively focused on establishing the chemical composition of reactive and nonreactive  $N_2O_4$  to a previously unattained degree.

The original specific objectives of the program were:

(1) To identify that constituent or component of  $N_2O_4$  that induces or enhances stress corrosion cracking (SCC) in 6Al 4V titanium alloy.

(2) To develop qualitative and quantitative methods of analysis that are capable of determining significant differences in various types of  $N_2O_4$ .

(3) To attempt to establish the possible presence of stress corrosion inhibitors in certain types of  $N_2O_4$  and to determine the concentration levels that are critical to their inhibitory action.

The general experimental approach consisted of the following steps:

(1) Development of a standard stress corrosion cracking test of sufficient sensitivity and statistical reliability to permit the assessment of the corrosive nature of different types of  $N_2O_4$ .

(2) Preparation of a variety of types of  $N_2O_4$  representing different reactivities with 6Al 4V titanium alloy and including:

a. Red-Reactive (RR)  $N_2O_4$ : Visually "red" material that induces SCC under standard test conditions.

b. Red-Nonreactive (RN)  $N_2O_4$ : Visually "red" material that does not induce SCC under standard test conditions.

c. Green  $N_2O_4$ : Visually "green" material representing the extremes of nitric oxide content of the MSC-PPD-2A specification, i.e., G4  $N_2O_4$  containing 0.4% NO and G8  $N_2O_4$  containing 0.8% NO.

(3) Analytical characterization of the above and other  $N_2O_4$  compositions, particularly with respect to measurable differences correlatable with SCC. It was recognized that this characterization would involve the development of new, sensitive, and precise methods for the determination of trace constituents of  $N_2O_4$  systems.

(4) Application of the standard SCC test, analytical methods, and compositional adjustment techniques in an effort to establish the critical concentrations of NO and H<sub>2</sub>O that must be added to reactive N<sub>2</sub>O<sub>4</sub> in order to prevent SCC.

This report summarizes the principal experimental investigations and presents the conclusions derived from the work performed during the contract period. Additional experimental details may be found in the quarterly reports. The more important test procedures and analytical methods have been compiled in the attached Appendix.

## DEVELOPMENT OF EXPERIMENTAL METHODS

### I. Standard Stress Corrosion Cracking Test

The standard stress corrosion cracking test developed for this program adhered closely to the minimum requirements defined in the original Request for Proposal. Basically, it consists of exposing stressed U-bend specimens of 6Al4V titanium alloy sheet to liquid N<sub>2</sub>O<sub>4</sub> at 165°F. for 72 hours in a glass-Teflon test cell. Ten specimens were exposed per test and failure was defined as the presence of visible breaks or cracks at the U-bend of the test specimen. Pertinent aspects of the test development are discussed below.

#### A. Test Materials

##### 1. Alloy

A single mill annealed sheet, 48 x 96 x 0.060-inches of 6Al4V ELI titanium was obtained from Titanium Metals Corp. It had acceptable chemical analysis and reasonably balanced physical properties including yield strength, tensile strength and elongation (Table 1). The sheet was ground to a 240-grit finish by Mill Products Corporation and protected with adhesive-backed paper before any was used for tests.

Blanks, 5-1/4 x 1 x 0.060-inches, were sheared from the sheet either transverse or parallel to the rolling direction. These were milled and drilled in the presence of 5% aqueous sodium nitrite coolant with the aid of suitable

TABLE 1 - CHEMICAL ANALYSIS AND PHYSICAL PROPERTIES  
OF 6Al4V ELI TITANIUM SHEET

Producer: Titanium Metals Corporation

Heat Treatment: Mill anneal, Heat No. G-4056, 8 hour car bottom  
anneal at 1350°F. followed by air cooling.

Chemical Analysis:

Element, % by Wt.						
<u>C</u>	<u>Fe</u>	<u>N</u>	<u>Al</u>	<u>V</u>	<u>H</u>	<u>O</u>
0.023	0.06	0.016	5.9	4.0	0.006	0.09

Physical Properties:

<u>Rolling Direction</u>	<u>Yield Strength psi.</u>	<u>Tensile Strength psi.</u>	<u>Elongation % in 2 inches</u>	<u>Bend Test (Radius x thickness)</u>
Longitudinal	136,900	147,700	14.5	4.0
Δ	2,200	1,300	-	-
Transverse	139,100	146,400	12.5	4.0

Surface Finish:

240 Grit on 4' x 8' x 1/16" Sheet (Mill Products Corp.)

jigs. The prebend blank developed at this point was  $5.000 \pm 0.002 \times 0.750 \pm 0.002 \times 0.060$  inches with two  $9/32$ " holes centered  $7/16$  inches in from either end. They were deburred by hand with 400 grit silicon carbide paper, then each was placed in a separate glassine envelope for protection. U-bends were made from the blanks on a modified No. 2 Di-Acro Bender with the aid of a 10-mil thick strip of Hi-fax 1900 polyethylene film to a 5t radius (0.30 inches).

The required measurements of lever arm, thickness, radius and initial spread were carried out for calculation of stress under load conditions. Following this, all bends were scrubbed with aluminum oxide until a water flash occurred. Any residual  $Al_2O_3$  was removed in subsequent water washes and acetone rinses. A final 5-minute boil in clean acetone, followed by drying with a hot air gun, completed the cleaning operation. Gum rubber gloves were employed during cleaning, and clean cotton gloves were used when clean and dry specimens had to be handled.

U-bends were deflected or loaded to the desired stress level by advancing a  $1/4$ -inch NC-20 nut on a bolt just prior to installation in a test cell. The deflections were calculated from a formula derived by Blake using a simple computer program. Results calculated from the Blake flat spring formula were compared with others in the literature and deformations of sample U-bends on a Tatnall testing

machine. Measurements made with bonded strain gages and micrometer showed no yielding had occurred when U-bends were loaded to 90% of yield strength using calculated deflections.

## 2. N<sub>2</sub>O<sub>4</sub> Test Material

Red-Reactive (RR) and Green 8 (G8) N<sub>2</sub>O<sub>4</sub> were each obtained in 1-ton cylinders from Hercules Incorporated, Hercules, California. The RR N<sub>2</sub>O<sub>4</sub> was produced to Mil-P-26539B specifications and the G8 N<sub>2</sub>O<sub>4</sub> near the upper nitric oxide limit (0.72% NO) of the MSC-PPD-2A specification. These cylinders were stored in a heated storage shed maintained at 80°F. to limit the possibility of a vacuum developing within the cylinders during cold weather. Cylinders were piped up with Type 304 SS pipe, tubing, valves and fittings so that either type of N<sub>2</sub>O<sub>4</sub> was available inside of a hood within the operating area.

### B. Test Cell Development

Corgard glass pipe, 3" I.D. x 12" L., was chosen for the test cell body because of adequate volume and resistance to operating pressure and temperature. Closures with adequate strength and compactness had to be developed. An initial end-closure design and modifications (Teflon blank flange containing a 1/8" NPT to Swagelok adapter and a Fisher-Porter glass valve) failed under cyclic pressure and temperature tests. Three runs were carried out with end-closures of 304 SS but metallic contamination might have



been excessive. Another attempt at a Teflon-glass end-closure resulted in the fabrication of an eccentric, 3" dia., pipe to 3/8" male tubing reducer. This was backed-up with a steel flange and the tubing could be connected to a Teflon or Fisher-Porter glass valve with a Teflon Swagelok connector. Neither the glass or Teflon valves were adequate for the job. A valve development program was then instituted and a few models made. These were tested under cyclic conditions and although much improved over the commercial models they were also not acceptable. Rather than jeopardize the test program further, type 304 SS, 3/8" needle valves were finally employed to seal off the tubing protrusion in the cell end closure. The combined assembly (Corgard pipe, Teflon eccentric reducers, back-up flanges and 304 SS needle valves) was used for 23 runs through the remainder of the SCC tests.

#### C. Establishment of Test Conditions

The RFP prescribed certain requirements for a satisfactory test procedure. The critical aspects of these

requirements were explored in a few tests with the following results:

Variable	Min. Req. per RFP	Experimental Result
Test Temp. Required for Cracking	165°F.	70-80°F.
Time to Crack at Req. Test Temp.	72 hours	<24 hours
Failure Definition	Visible breaks or cracks at the U-bend.	Stress cracks also occurred at identification stampings, near sheared edges, worked areas and at spot welds.
Number of Specimens	10	Exposure of 255 specimens in 26 runs resulted in 100% consistency of failures or passes in every run.

Because some of the test requirements were not highly critical, variations were permitted in test time,  $72 + \frac{4}{12}$  hrs., and temp.,  $165 \pm \frac{5}{3}$  °F.

Test cell loading, sampling, and emptying presented few problems once a satisfactory design was developed and because of pressure tests before each run. All cells, with specimens in place, were first tested for N<sub>2</sub> leakage under water at 18 psig. A satisfactory bubble rate, >5 seconds per bubble, had to be maintained for 5 minutes before the cell was deemed satisfactory for introduction of N<sub>2</sub>O<sub>4</sub>. Samples were obtained by warming the filled test cell to force liquid N<sub>2</sub>O<sub>4</sub> into a standard 50 or 100 ml. sample bulb. An ullage of 85%

was employed before exposure of each cell. After each test, the  $N_2O_4$  was sampled then emptied into a 9-gallon SS "Oxygen Bomb" before final transfer to a 1-ton cylinder used as a waste receiver.

#### D. Specimen Examination - Failure Determination

Specimens were given an examination ranging from a cursory look under a stereomicroscope to a rather probing search for cracks at 400X. All specimens with obvious cracks were checked for a rough estimate of crack density and to see if identification stampings also had cracks. When the crack density of U-bends was to be determined, a line intercept approach was used. At least two observers checked each individual specimen that had not obviously cracked. Such specimens were examined under stressed and unstressed conditions at magnifications up to 400X. No examination of specimens prepared by metallographic techniques was attempted since the milled edges and 240 grit specimen surface were adequate for crack determination.

### II. Preparation and Testing of Specified Types of $N_2O_4$

#### A. Red Reactive (RR) $N_2O_4$ , Mil-P-265359B Specification

The  $N_2O_4$  of Mil-P-265359B quality was quickly shown to be Red Reactive (RR)  $N_2O_4$ . It thus became the basic type

for exploring rolling orientation, stress level, temperature and time requirements with respect to SCC. With RR  $N_2O_4$  it was shown that:

1. Specimens oriented transverse or longitudinal to the rolling direction had an equal propensity for cracking.

2. Stress levels which would produce cracking could be the residual stress left after shearing, stresses produced forming U-bends or 30% of the yield strength (41,000 psi.) with loaded U-bends.

3. The temperature required for cracking could be as low as 70-80°F. for a 76-hour test period.

4. Exposure of U-bends at 162°F. would result in cracks in <24 hours.

The number of specimen failures was always equivalent to the number exposed, 70/70.

B. Red Nonreactive (RN)  $N_2O_4$

In the context of this program, Red Nonreactive (RN)  $N_2O_4$  is defined as material that is visually indistinguishable from RR  $N_2O_4$  at 0°C. and which does not cause SCC in the standard test. At the beginning of this program, no such material was available. However, preliminary work indicated that it was possible for a sample to be visually red and still contain significant amounts of NO. Subjective visual assessments of color are influenced by the temperature

dependence of the  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  equilibrium, the depth of the solution observed, and basic red-green color sensitivity.

Various proportions of prechilled RR and G8  $\text{N}_2\text{O}_4$  were mixed and allowed to equilibrate in an ice bath. The mixtures represented a series containing approximately 0, 400, 800, and 8000 ppm. NO. A panel of five individuals examined the mixtures and none could distinguish the 400 ppm. NO sample from RR  $\text{N}_2\text{O}_4$ . Two of the five claimed to detect a greenish cast in the 800 ppm. sample. Thus, it was concluded that any sample of visually red  $\text{N}_2\text{O}_4$  might contain as much as 800 ppm. NO. A mixture of RR and G8  $\text{N}_2\text{O}_4$  was prepared and found to contain 500 ppm. NO. The sample was visually red at 0°C. Failure rate in the SCC test was 0/10.

Later in the program, a different type of RN  $\text{N}_2\text{O}_4$  was obtained and subjected to SCC testing and analysis. The results will be described in a later section.

C. G8  $\text{N}_2\text{O}_4$ , MSC-PPD-2A Specification

Type G8  $\text{N}_2\text{O}_4$  with 7200 ppm. NO did not crack any of 20 U-bend specimens stressed at 90% of the yield strength (123,000 and 125,000 psi.) and formed with 5t radius. Failure rate 0/20.

D. G4  $\text{N}_2\text{O}_4$ , MSC-PPD-2A Specification

No cracks were found in 10 U-bends exposed to this material which resulted from a blend of RR and G8  $\text{N}_2\text{O}_4$ .

### III. Composition Adjustment - Technique Development

#### A. Removal of Protonated Species from $N_2O_4$

The "dehydration" or reduction of the concentration of protonated species in RR  $N_2O_4$  was essential to the critical-level study of the inhibition of SCC by the addition of NO and/or  $H_2O$ . Early laboratory work showed that the passage of RR  $N_2O_4$  vapors through a column filled with activated Linde Molecular Sieve Type 3A followed by condensation at  $0^\circ C$ . could produce liquid  $N_2O_4$  containing some NO, but greatly reduced in proton concentration. This basic procedure was scaled-up in a unit capable of producing approximately 1 to 1.5 liters/hour of "dehydrated"  $N_2O_4$ . During this same period, near-infrared analytical work showed that  $HNO_3$  is essentially the only protonated compound present in RR  $N_2O_4$ . Therefore, using this measurement of  $HNO_3$  as an index of "dehydration", it was found that approximately 95% of the protonated species could be removed in this unit. Starting material containing about 6,000 ppm.  $HNO_3$  was routinely reduced to below 500 ppm. and usually below 300 ppm. Considering the fact that the system involved transfers from the dry  $N_2O_4$  receiver to SCC test cells and/or sample bulbs under ambient high-humidity conditions, these results were considered to be satisfactory.

Capacity of the 3A Molecular Sieve for the "dehydration" of  $\text{N}_2\text{O}_4$  was not determined accurately. However, preliminary estimates are of the order of 2 ml.  $\text{N}_2\text{O}_4/\text{cm}^3$  Molecular Sieve based on 55% vaporization of the charge. At lower initial  $\text{HNO}_3$  levels, or with multipass drying, the capacity should be considerably greater. Lower initial  $\text{HNO}_3$  levels should be achievable by rectification through 5-10 theoretical plates at moderate reflux ratios prior to passage through the adsorbent. The use of other types of adsorbents may also be indicated. Since the protonated material to be removed is primarily  $\text{HNO}_3$ , activated alumina or other types of Molecular Sieve may offer some advantages.

In all instances in which  $\text{N}_2\text{O}_4$  was passed through an activated Molecular Sieve column, a small amount of nitric oxide was produced. Often the initial  $\text{N}_2\text{O}_4$  condensate was green, indicating an NO content of >1,000 ppm. The source of the NO is probably from reaction of  $\text{NO}_2$  with tightly bound water in the sieve crystal or with adsorbed water incompletely removed by the activation process. Nitric oxide may also be generated by reaction of  $\text{HNO}_3$  with the basic sieve material to form water which will then react with additional  $\text{NO}_2$ . In cases when it is desired to produce a "dry", NO-free sample, the NO ( $\text{N}_2\text{O}_3$ ) must be removed by reaction with gaseous oxygen.

An additional dimension of purification is provided by the Molecular Sieve "dehydration" procedure. It was found that the trace metals content of  $N_2O_4$  was significantly reduced by this process. For example, the iron content of a typical sample of RR  $N_2O_4$  was reduced from 0.3 ppm. to about 0.04 ppm. Fe.

#### B. Deoxygenation of $N_2O_4$

The removal of dissolved oxygen from  $N_2O_4$  was attempted either by vapor purging or by chemical reaction. In both cases, the extent of deoxygenation was followed by gas chromatography. It was found to be simpler and more effective to react the  $O_2$  with NO or with "green"  $N_2O_4$  rather than perform a series of vapor purges and equilibrations. Gas chromatographic analysis indicated that the amount of dissolved  $O_2$  could be decreased by this latter treatment to well below 1 ppm.

#### C. Add-Back Techniques

Hypodermic syringe techniques were used for essentially all of the add-back experiments reported here. By this approach, for example, 1,400 cc. of NO was transferred in 100 cc. portions through a silicone rubber septum into one corrosion test cell with minimal water contamination. In other experiments, NO as well as  $H_2O$  and  $O_2$  have been added to test cells. The septums are usable for two days when in



contact with  $\text{N}_2\text{O}_4$  vapors at ambient temperatures. After this period they begin to harden and crack and lose ability to seal against the hypodermic needles. In liquid  $\text{N}_2\text{O}_4$  they do not last much longer than ten minutes. Because of the marginal utility of silicone rubber, other more resistant rubbers, e.g., Viton or other fluorocarbon elastomer, should be tested for this application.

#### IV. Development of Analytical Methods

All of the  $\text{N}_2\text{O}_4$  involved in the stress corrosion cracking of titanium alloys has been high purity material, i.e., >99%. Consequently, the analytical development effort, designed to establish compositional differences between different types of  $\text{N}_2\text{O}_4$ , was entirely devoted to the quantitative determination of minor and trace constituents. The need for highly sensitive and precise analytical methods was emphasized by the known fact that stress corrosion cracking in other systems can be initiated and/or inhibited by very low concentrations of various chemical species. In addition, it was felt that the measurement of minor changes occurring in the composition of  $\text{N}_2\text{O}_4$  during and after stress corrosion cracking tests might provide some insight into the mechanisms of attack and inhibition. The principal experimental

efforts were directed toward the development of analytical methods for the determination of the following:

- A. Combined nitric oxide
- B. Protonated species
  - 1. Total proton content
  - 2. Distribution of individual protonated compounds
- C. Dissolved oxygen and other gases
- D. Combined chlorine
- E. Metallic impurities

The major aspects of each development will be discussed below.

A. Combined Nitric Oxide

Nitric oxide dissolved in  $N_2O_4$  reacts with equilibrium amounts of  $NO_2$  to form  $N_2O_3$ . Measurement of the intensity of the visible absorption band of  $N_2O_3$  at 700 m $\mu$  provides an accurate and precise measurement of combined NO in  $N_2O_4$ . The method requires a specially designed cell constructed of materials resistant to  $N_2O_4$ , capable of operation at subambient temperatures, and leakproof under moderate pressure and vacuum. In its original version (1), the method was designed to determine NO at the 0.2-1.5% level using a 2 mm. pathlength and an operating temperature near 0°C. It was felt that the operating range of the method could be extended to lower concentration by using lower temperatures to reduce

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(1) C. M. Wright, A. A. Orr, and W. J. Balling, Anal. Chem., 40, 29 (1968).

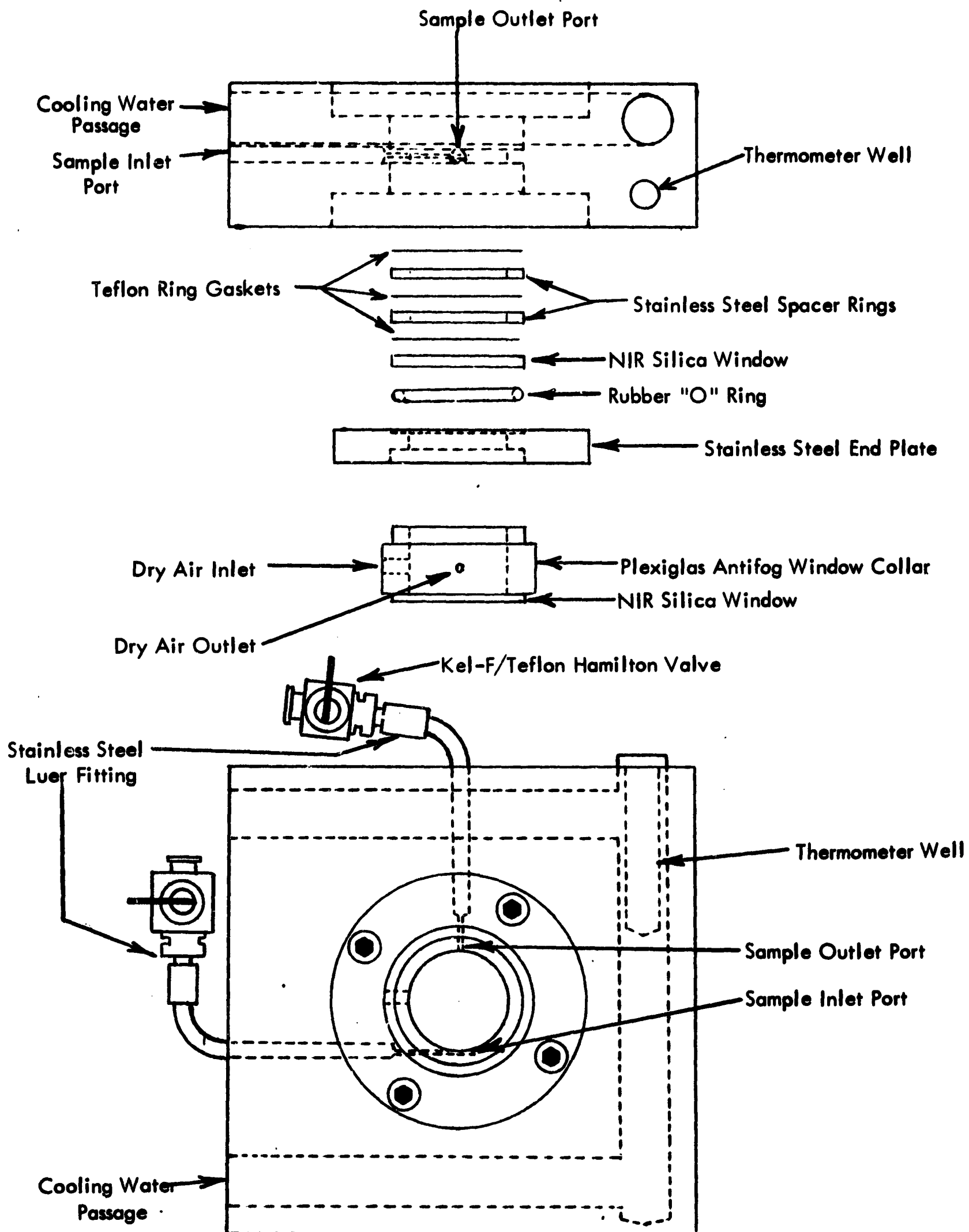
the background absorption of  $\text{NO}_2$ , by increasing the cell pathlength, and by employing an expanded scale slide-wire in the spectrophotometer.

Lower operating temperatures were obtained by the use of refrigerated circulating bath (Forma Model 2095-2), This bath was capable of rapidly cooling the cell and maintaining an operating temperature of  $-10.0 \pm 0.2^\circ\text{C}$ . Adjustment of the cell path length to approximately 10 mm. was readily accomplished because this capability had been incorporated into the original design. However, because of the decrease in operating temperature from about  $0^\circ\text{C}$ . to  $-10^\circ\text{C}$ ., the original antifogging system was found to be inadequate. The problem was eliminated by attaching "storm windows" to the outside of each cell window. These consisted of 1/2-inch thick Plexiglas collars fitted with thin silica windows and drilled with small holes to permit a slow purge of dry gas between the cell windows and the "storm windows" (Figure 1). Installation of a new 10X scale expansion slide wire in a Cary Model 14 spectrophotometer completed the analysis system.

The above system was used to study the background absorption of NO-free  $\text{N}_2\text{O}_4$  at  $-10^\circ\text{C}$ ., determine the limit of detection of the method, and establish quantitative calibration curves over the desired operating ranges. It was found that  $\text{N}_2\text{O}_4$  contributed a small, reproducible net background absorbance

- 29 -  
Figure 1

Spectrophotometric Cell



at the measuring wavelength of about 0.005-0.010 absorbance units. During this work, a new reference wavelength of 900 mμ was selected for absorbance measurements. The limit of detection of the method was estimated to be approximately 15 ppm. NO. Calibration curves were found to be linear in the working range studied, and the analysis of low level known mixtures agreed well with previously established absorptivity values.

It was concluded that:

1. NO can be determined in the 0.3-2.0% range using a 2 mm. pathlength and a 0-2.0 absorbance scale with a relative standard deviation of 0.5-3%.

2. NO can be determined in the 400-4000 ppm. range using a 10 mm. pathlength and a 0-2.0 absorbance scale with about the same precision.

3. NO can be determined in the 15-400 ppm. range using a 10 mm. pathlength and a 0-0.2 absorbance scale. Precision is estimated to be  $\pm 15$  ppm. in this range.

A detailed procedure is given in the Appendix.

## B. Protonated Species

### 1. Total Proton Content

At the beginning of this work, the nature of the protonated species in equilibrium with various types of liquid N<sub>2</sub>O<sub>4</sub> was not known. Therefore, a method was sought that was capable of measuring total proton content without regard for

the actual nature of the molecular species present. The obvious choice was nuclear magnetic resonance, since the protons in all of the anticipated compounds ( $\text{H}_2\text{O}$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ) would be expected to exchange rapidly and form a single peak in the NMR spectrum. The area of this peak would be proportional to the concentration of protons present and therefore could be used for quantitative measurements. This approach was extensively investigated.

In the development of an NMR method for the determination of total proton content, it was decided to employ an internal standard technique. Such a technique offers significant advantages of simplicity and improved accuracy over other calibration methods. In a recent publication, Saraf and Fatt (2) describe a variation in the sensitivity of NMR detection of  $\text{H}_2\text{O}$  in a variety of liquid systems. Normally, the area of an NMR peak is assumed to vary linearly with the concentration of absorbing protons in the sample, and a calibration factor (K) calculated for a known sample may be used as a calibration for the analysis of an unknown sample of similar composition. Saraf and Fatt, however, showed that K varied with the ionic conductivity of the sample. This effect was shown to be due to a variation of the quality factor, Q, of the sample

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(2) D. N. Saraf and I. Fatt, Nature, 214, 1219 (1967).

detector coil with the conductivity of the sample, and can cause a significant error in the determination of water in samples which are chemically similar but differ in conductivity. This is of importance in  $N_2O_4$  analysis, since the conductivity of  $H_2O$ -containing  $N_2O_4$  samples varies with the water content. Thus, a calibration series of samples of increasing water content would be expected to have a varying  $K$ . For this reason, when a plot of peak area vs. % added water is prepared, the extrapolation to zero added water would not give an accurate value for the amount of water originally in the sample.

This problem is avoided in the internal standard procedure since, in a given sample, the  $Q$  factor will be the same for the  $H_2O$  and internal standard peaks, and the area/concentration factor will therefore be the same for both peaks. Benzene was selected as the internal standard in this work.

a. Spectral Characteristics of the  $N_2O_4$ - $H_2O$  System

When an NMR peak is caused by a proton which is rapidly exchanging between two or more different chemical environments, the chemical shift of the observed peak will depend on the relative concentrations of the exchanging species. Thus, the chemical shift of the "water peak", which is actually due to the protons on  $H_2O$ ,  $HNO_2$ , and  $HNO_3$ , will be given by the expression:

$$\Delta_{ave} = M_{H_2O} \Delta_{H_2O} + M_{HNO_2} \Delta_{HNO_2} + M_{HNO_3} \Delta_{HNO_3}$$

where  $M_x$  is the mole fraction of species  $x$  in the mixture and  $\Delta_x$  is the chemical shift of the  $x$  peak with respect to the benzene internal standard. In addition, the shape of the average peak for an exchanging system varies with the rate of the exchange reaction and relative concentration of the components. Because of these effects, an important difference between the spectral characteristics of "red" and "green" samples of  $N_2O_4$  was noted. Samples of the bulk tank samples of red (RR) and green (G8)  $N_2O_4$ , which were found to contain approximately the same amount of water ( $0.090 \pm 0.01\%$ ) were observed to give distinctly different peak shapes for the  $H_2O$  peak. In analyzing a number of aliquots of both samples, the red  $N_2O_4$  was always observed to give a relatively sharp, narrow peak, with a line width at half-height ( $\nu_{1/2}$ ) of  $\approx 2$  Hz. The green  $N_2O_4$ , however, gave a broad, poorly defined peak, with  $\nu_{1/2}$  in the range of 8-12 Hz. This would suggest that the species participating in the equilibrium reaction which gives rise to the so-called "water peak" in  $N_2O_4$  are exchanging much more rapidly in the red  $N_2O_4$  than the green. When additional water is added to the samples, the peak in the green sample becomes narrower and at  $>0.2\%$   $H_2O$  is similar to that observed in red  $N_2O_4$ . In both samples  $\Delta_{H_2O}$  decreases as  $C_{H_2O}$  increases (the peaks shift to higher field).



Typical spectra of "red" and "green"  $\text{N}_2\text{O}_4$  samples are given in Figures 2 and 3, respectively.

b. Quantitative Results - Precision and Accuracy

The accuracy of the method was evaluated by the analysis of  $\text{N}_2\text{O}_4$  samples to which known amounts of water had been added. In the range of 0.1 to 0.5% water, agreement between "added" and "found" values was usually within 0.01-0.02%.

The precision of the NMR procedure was determined by replicate analysis of several different types of  $\text{N}_2\text{O}_4$  containing 0.03-0.2%  $\text{H}_2\text{O}$ . The standard deviation was found to be approximately 0.004%  $\text{H}_2\text{O}$ .

Time averaging of the spectrum, which increases the signal-to-noise ratio, should thus result in a more precise analysis. In order to demonstrate this improvement, and to prove that the limit of detection of the method could be extended to the 0.01%  $\text{H}_2\text{O}$  level, a sample found to contain 0.0360%  $\text{H}_2\text{O}$  by the single scan method ( $S = 0.0037$ ), was reanalyzed using a time-averaged spectrum obtained by summing fifty scans of the sample. In this experiment, the benzene peak was used to trigger the repetitive scan, and a smaller amount of nitrobenzene was added as an internal standard. Typical single scan and time-averaged spectra are shown in Figure 4. The time-averaged data gave %  $\text{H}_2\text{O} = 0.0393$  with  $S = 0.0007$ , or a relative standard deviation of 1.8%. The signal-to-noise level of the time-averaged spectrum in

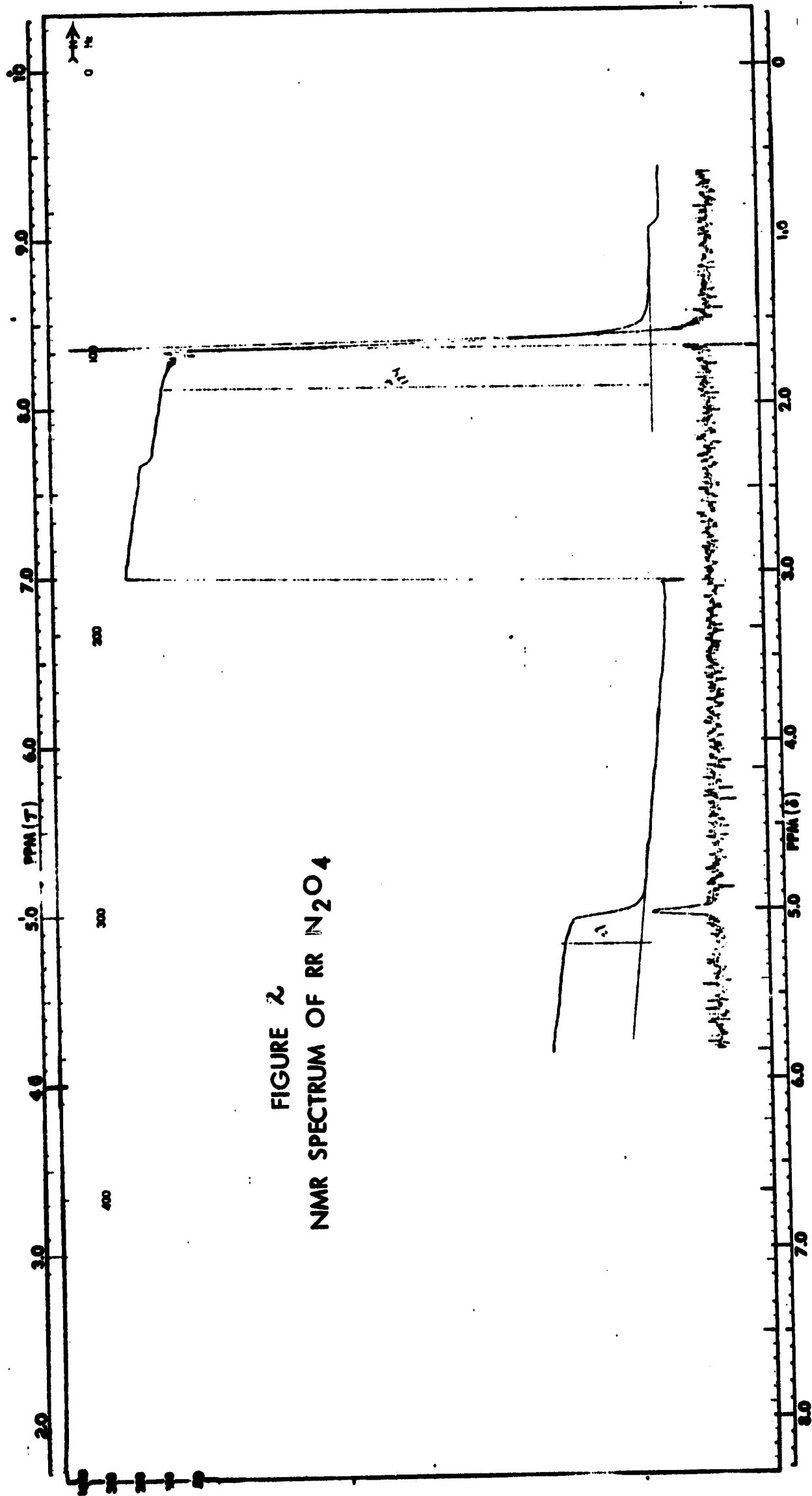


FIGURE 2  
NMR SPECTRUM OF RR N<sub>2</sub>O<sub>4</sub>

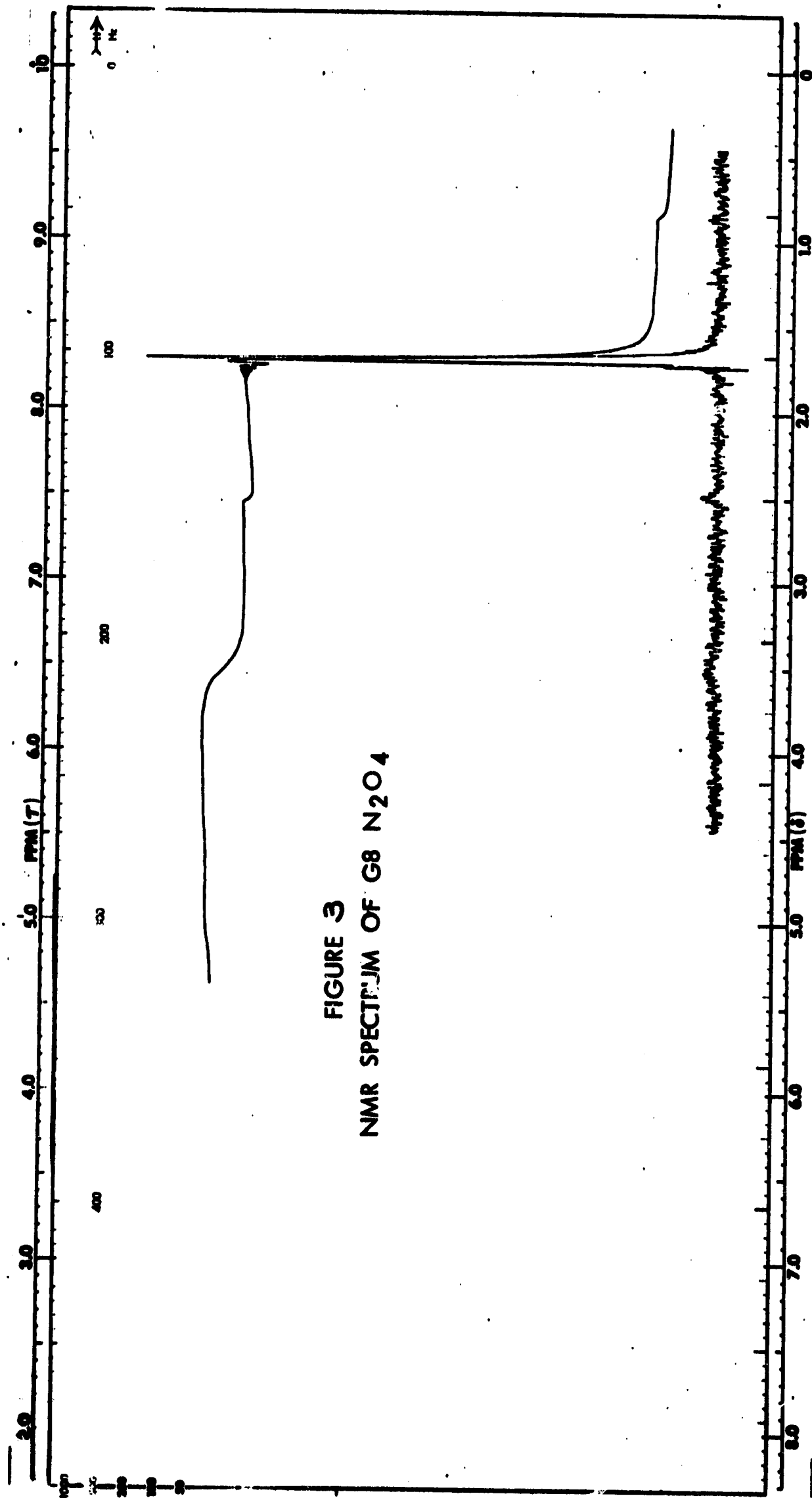
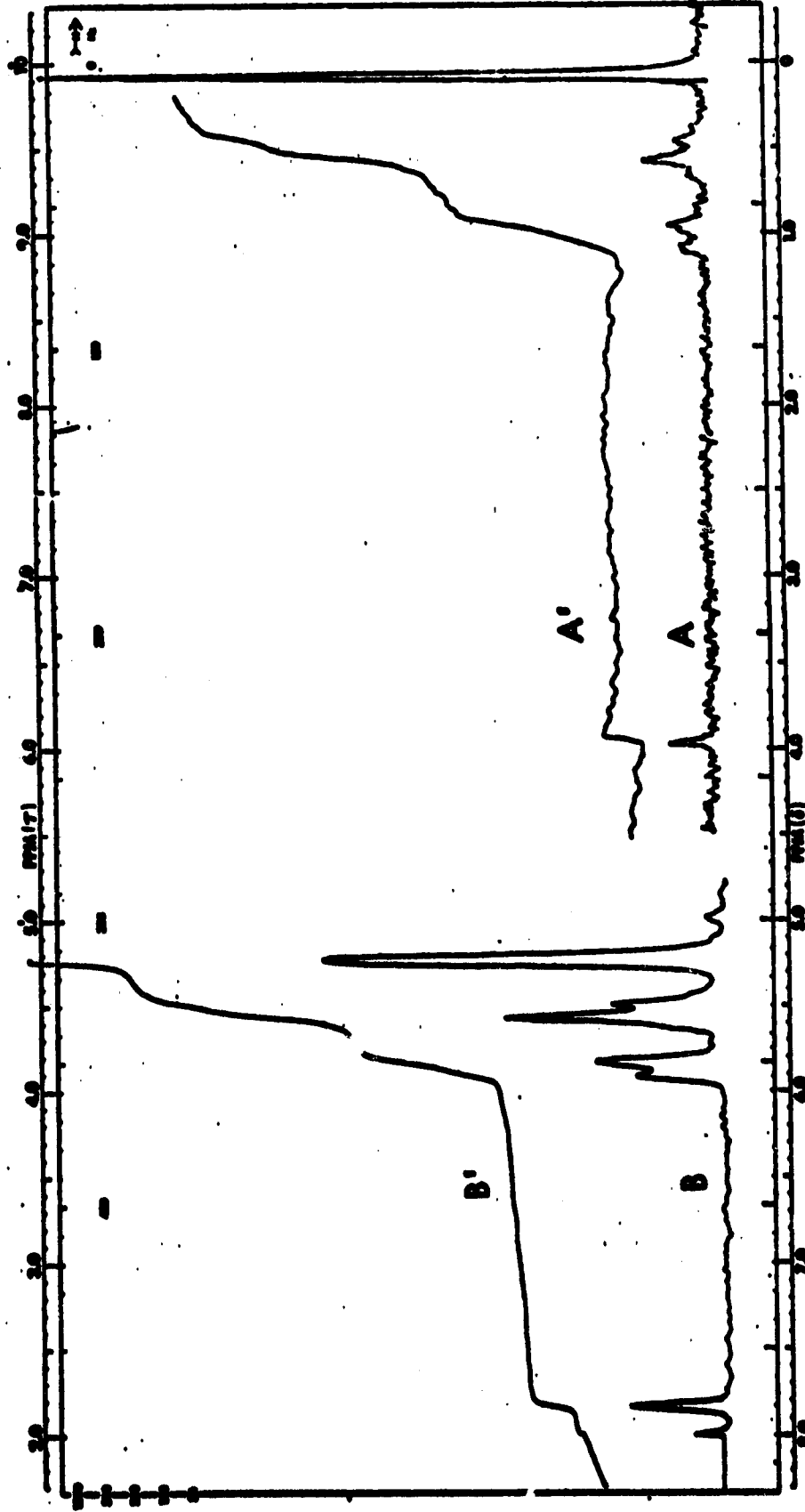


FIGURE 3  
NMR SPECTRUM OF G8 N<sub>2</sub>O<sub>4</sub>

FIGURE 4

NMR SPECTRUM OF 0.039% H<sub>2</sub>O IN N<sub>2</sub>O<sub>4</sub>

- Curve A - Single Scan
- Curve A' - Integral of A
- Curve B - Time Average of 50 Scans
- Curve B' - Integral of B



60 MHz NMR

Spectrum No.: 1906

Operator: G. A. Ward

Date: December 5, 1967

Sample: X 16078-16

(A)

Solvent: None

Temperature: 10°C.

Filter Bandwidth: 1 Hz

R.F. Field: .02 mG

Sweep Time: 250 sec.

Sweep Offset: --

Spectrum Amp.: 40

Integral Amp.: 40

Remarks:

(B) = Time Average of  
50 Scans of A.

Sweep Time = 100 sec.

Scan Width = 300 Hz

Read Out in 100 sec.,

with ST = 250

Figure 4 is obviously high enough to permit reliable detection, if not measurement, of 0.01% water, since a peak one-fourth as high as the observed one would still give a signal-to-noise ratio of nearly four to one.

This spectrum was obtained using a sweep time of 100 sec., so that the analysis time, including sample preparation and calculation is increased to nearly two hours, with approximately 90 minutes of spectrometer time required for each run.

A potential source of error which could not be estimated by add-back experiments is that due to water adsorbed on the surface of the NMR tubes. This effort was studied and it was found that a maximum amount of 0.19 mg. of water could be contributed from the sample tube and sampling system. This corresponds to 0.01% in a typical 2 g.  $\text{N}_2\text{O}_4$  sample. This was not considered significant for analyses at the 0.1% level, but it indicated that special precautions were necessary for trace analyses.

It was concluded from the above work that the developed NMR method gave adequately precise and accurate results for samples containing >0.05% water. At this level, relative standard deviation of 5-10% could readily be obtained. The method is easily extended to samples containing 0.01% water by computer time-averaging of the sample spectrum, but at a cost of considerably increased spectrometer time per sample. A detailed procedure is included in the Appendix.

## 2. Distribution of Protonated Species

It was originally proposed that the equilibrium proton exchange process that occurs between protonated species in  $\text{N}_2\text{O}_4$  might be significantly slowed by cooling  $\text{N}_2\text{O}_4$ -solvent mixtures to low temperatures. NMR could then be used to observe and measure the individual protonated species. Attempts to resolve the peaks of the protonated species from each other by operation at temperatures down to  $-80^\circ\text{C}$ . were unsuccessful. The main difficulties encountered in this work included the selection of a suitable solvent, phase separations during cooling, and the fact that very low temperatures (below  $-80^\circ\text{C}$ .) appeared to be required to alter the exchange process. The failure of this approach was more than compensated for by the success achieved, late in the program, from spectroscopy studies. An early paper (3) on vapor phase near-infrared (NIR) spectra of  $\text{HNO}_3$  and  $\text{HNO}_2$ , led to an investigation of the NIR region of the absorption spectrum as a possible source of information concerning the nature and distribution of the protonated species in  $\text{N}_2\text{O}_4$ .

Preliminary results were very encouraging. Examination of the absorption spectra of liquid  $\text{N}_2\text{O}_4$  samples in the  $1.3\text{-}1.6\mu$  region revealed definite differences between

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(3) E. J. Jones, J. Am. Chem. Soc., 65, 2274 (1943).

RR and G8  $\text{N}_2\text{O}_4$ . The spectrum of RR  $\text{N}_2\text{O}_4$ , containing about 850 ppm. "water", showed only one characteristic band at  $1.47\mu$ . The spectrum of G8  $\text{N}_2\text{O}_4$ , also containing about 850 ppm. "water", showed the same  $1.47\mu$  band, a shoulder at about  $1.45\mu$ , and an additional well-resolved band at  $1.405\mu$ . Additional scanning of the G8 spectrum revealed the presence of another band at  $1.90\mu$  that was not present in RR  $\text{N}_2\text{O}_4$ .

A sample of RR  $\text{N}_2\text{O}_4$  was dried by distillation through a column of 3A Molecular Sieve and treated with  $\text{O}_2$  to remove traces of NO. Very little absorption was observed in the  $1.35\mu$  to  $1.55\mu$  region. Addition of a small amount of water to this sample caused the appearance of the  $1.405$ ,  $1.47$ , and  $1.90\mu$  bands. The presence of the shoulder at  $1.45\mu$  could not be established with certainty.

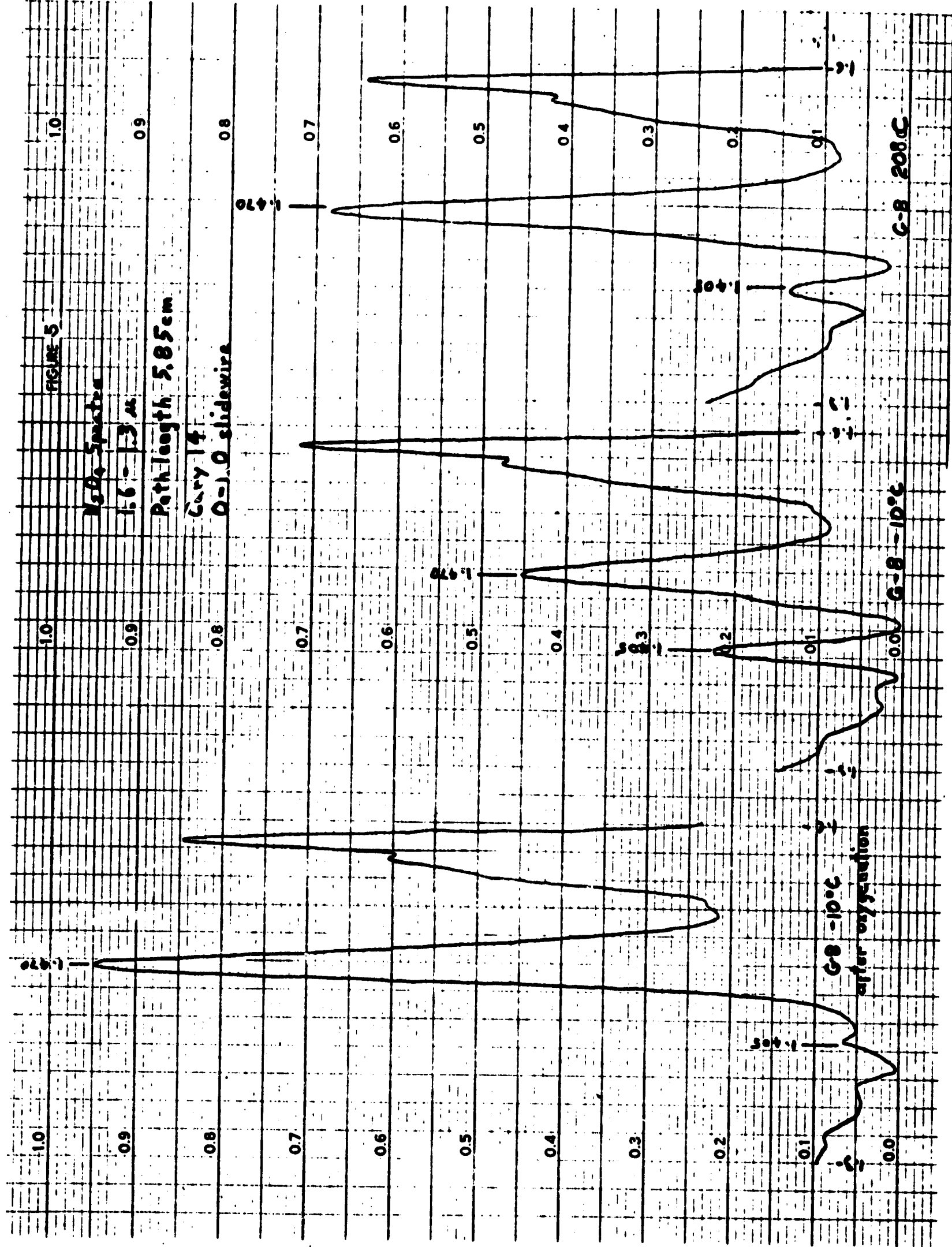
$\text{D}_2\text{O}$  was added to another sample of the dried RR  $\text{N}_2\text{O}_4$  and it was observed that the sample turned green, but no bands developed in the  $1.4$ - $1.5\mu$  region. The  $1.405$ ,  $1.47$ , and  $1.9\mu$  bands had shifted to  $1.89$ ,  $1.92$ , and  $2.56\mu$ , respectively, which indicated that all three of these original bands were due to protons and were probably OH stretch overtones of different molecular species. The  $1.9\mu$  band observed in wet green  $\text{N}_2\text{O}_4$  falls where the OH stretch-HOH deformation combination band of  $\text{H}_2\text{O}$  should be, and since no other compound has two hydrogens on a single oxygen, this band is considered to be unique to water. Oxygenation of G8  $\text{N}_2\text{O}_4$  simultaneously

eliminated the 1.405, 1.45, and 1.9 $\mu$  bands and enhanced the 1.47 $\mu$  band. The relative intensities of the 1.405, 1.45, and 1.47 $\mu$  bands were also found to be temperature dependent (see Figure 5). The 1.47 $\mu$  band was definitely assigned to HNO<sub>3</sub> by an experiment in which 99% HNO<sub>3</sub> was added to dry N<sub>2</sub>O<sub>4</sub>. A series of additions of 99% HNO<sub>3</sub> produced a calibration curve suitable for quantitative measurements.

Although the oxygenation experiment suggested that the 1.405 $\mu$  band was due to HNO<sub>2</sub>, additional proof was required. Approximately 0.5 ml. of liquid N<sub>2</sub>O<sub>3</sub> was added to about 50 ml. of RR N<sub>2</sub>O<sub>4</sub> in a glass bulb, and the resulting mixture scanned. The 1.47 $\mu$  band decreased and the 1.45 $\mu$  shoulder and 1.405 $\mu$  band appeared. Further addition of N<sub>2</sub>O<sub>3</sub> caused the 1.45 $\mu$  shoulder to become a definite band with further decrease of 1.47 $\mu$  band. With this evidence, it was then suspected that the 1.45 $\mu$  band might be HNO<sub>2</sub> and that the 1.405 $\mu$  band might be due to H<sub>2</sub>O.

In an attempt to generate HNO<sub>2</sub> under simplified equilibrium conditions, a new approach was tried. A water-saturated sample of CCl<sub>4</sub> was first scanned in a standard 10 cm. cell using the 0-0.2 absorbance slidewire. The NIR spectrum showed two water bands at 1.89 $\mu$  and 1.395 $\mu$  (Figure 6) comparable to the 1.90 $\mu$  and 1.405 $\mu$  bands observed in G8 N<sub>2</sub>O<sub>4</sub>. Since N<sub>2</sub>O<sub>3</sub> is the anhydride of nitrous acid,





addition of  $N_2O_3$  to the wet  $CCl_4$  should generate only  $HNO_2$  at the expense of the water present. A small amount of liquid  $N_2O_3$  was added to the wet  $CCl_4$  and the mixture scanned. The 1.89 and 1.395 $\mu$  water bands disappeared and a new band at 1.445 $\mu$  appeared (Figure 7) comparable to the 1.45 $\mu$  band in  $N_2O_4$ . Addition of  $N_2O_3$  to dry  $CCl_4$  showed only a weak 1.45 $\mu$  band probably due to a small amount of water in the "dry"  $CCl_4$ , but definitely showing that the band was not due to  $N_2O_3$  per se (Figure 9). Addition of 99%  $HNO_3$  to dry  $CCl_4$  showed a band at 1.465 $\mu$ , comparable to the 1.47 $\mu$  band in  $N_2O_4$ . An additional experiment in which successive alternate additions of small amounts of liquid  $N_2O_3$  and  $N_2O_4$  to wet  $CCl_4$  showed the 1.445 $\mu$  band increased and the 1.465 $\mu$   $HNO_3$  band decreased with addition of  $N_2O_3$  while the opposite was true for addition of  $N_2O_4$  (Figure 8). The 1.395 $\mu$  and 1.89 $\mu$  water bands decreased only slightly through the course of the additions.

On the basis of the above experiments, the four bands have now been assigned as follows:

1.405 $\mu$	$H_2O$	OH stretch overtone
1.45 $\mu$	$HNO_2$	OH stretch overtone
1.47 $\mu$	$HNO_3$	OH stretch overtone
1.90 $\mu$	$H_2O$	OH stretch-HOH deformation combination

A spectrum of  $N_2O_4$  containing all four bands is shown in Figure 10.

Figure 6

Figure 7

Figure 8

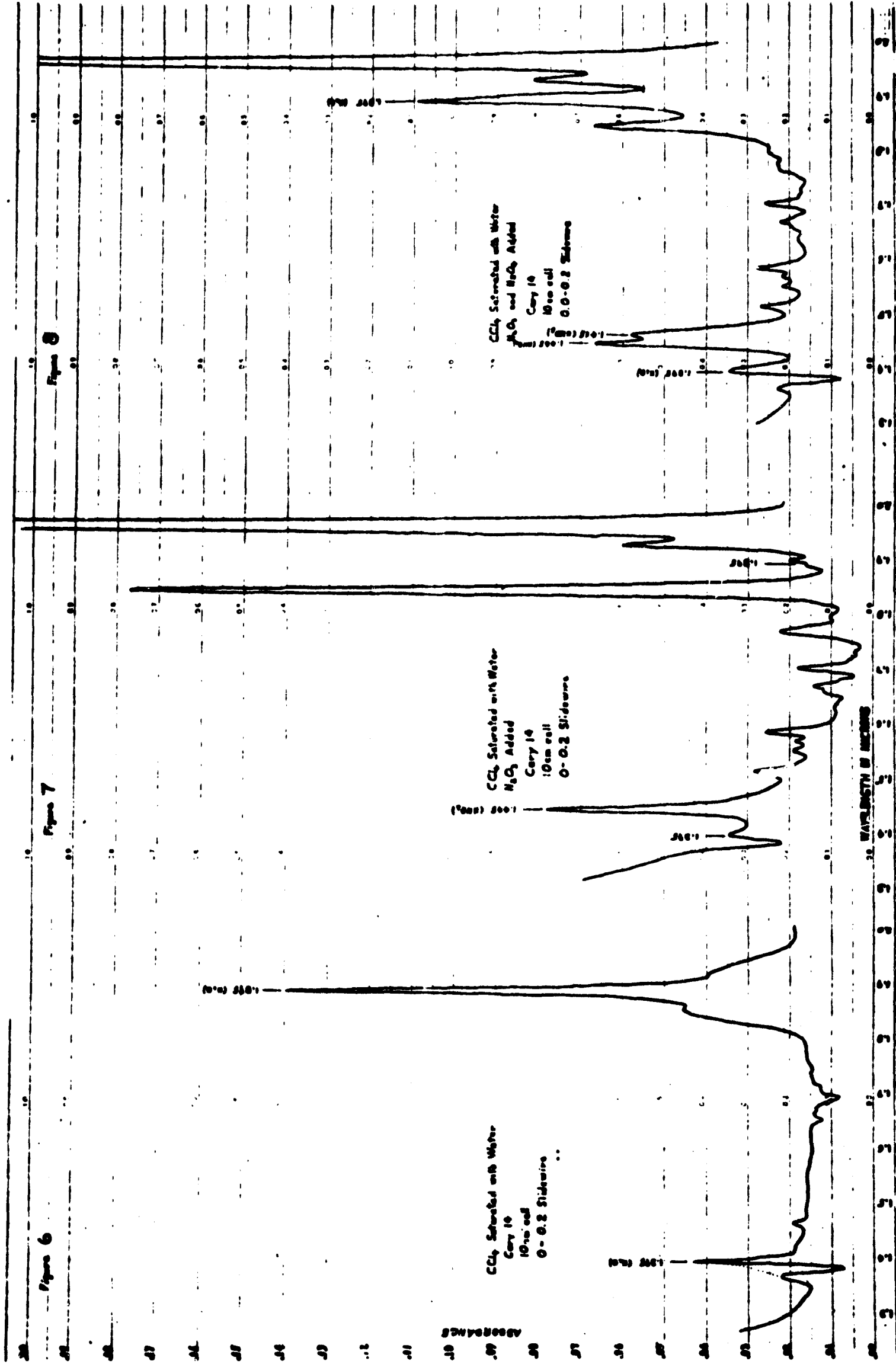
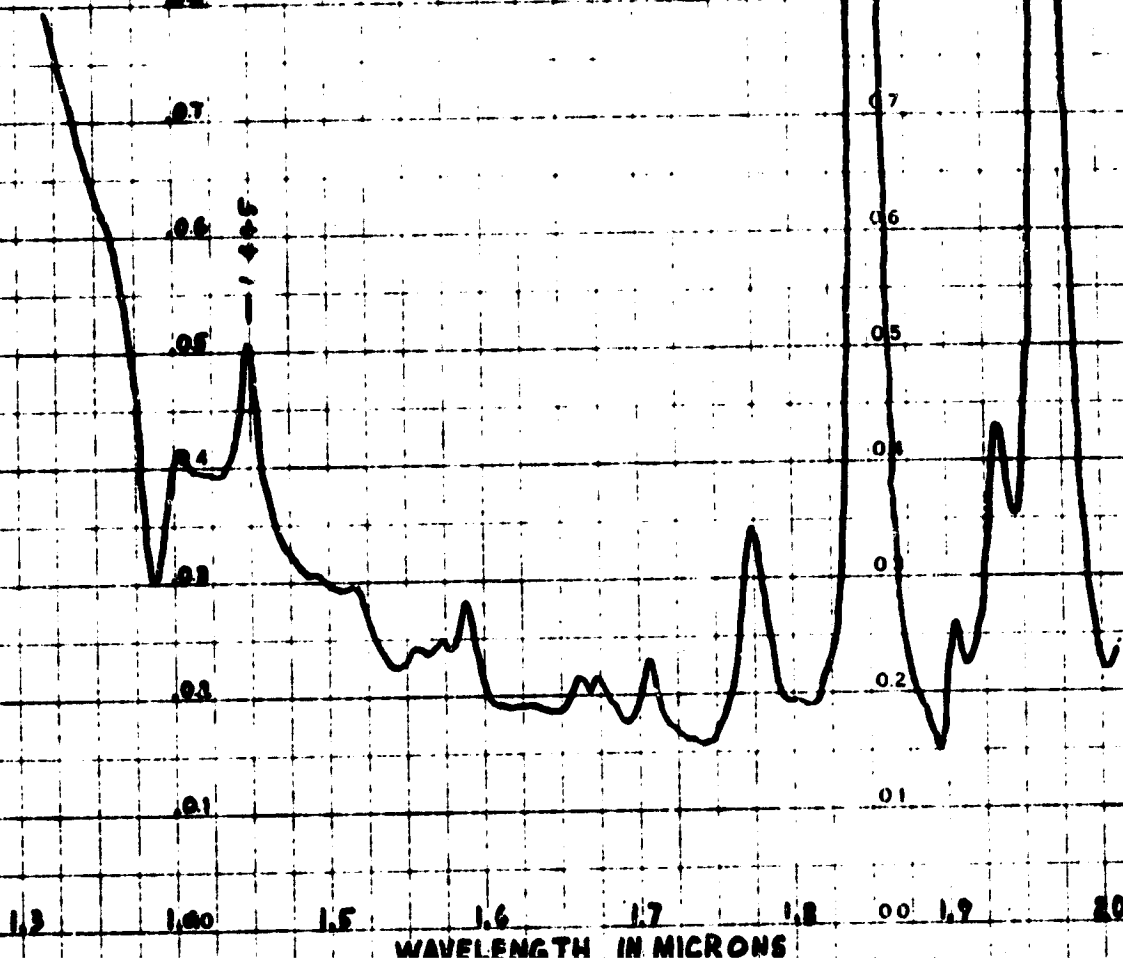
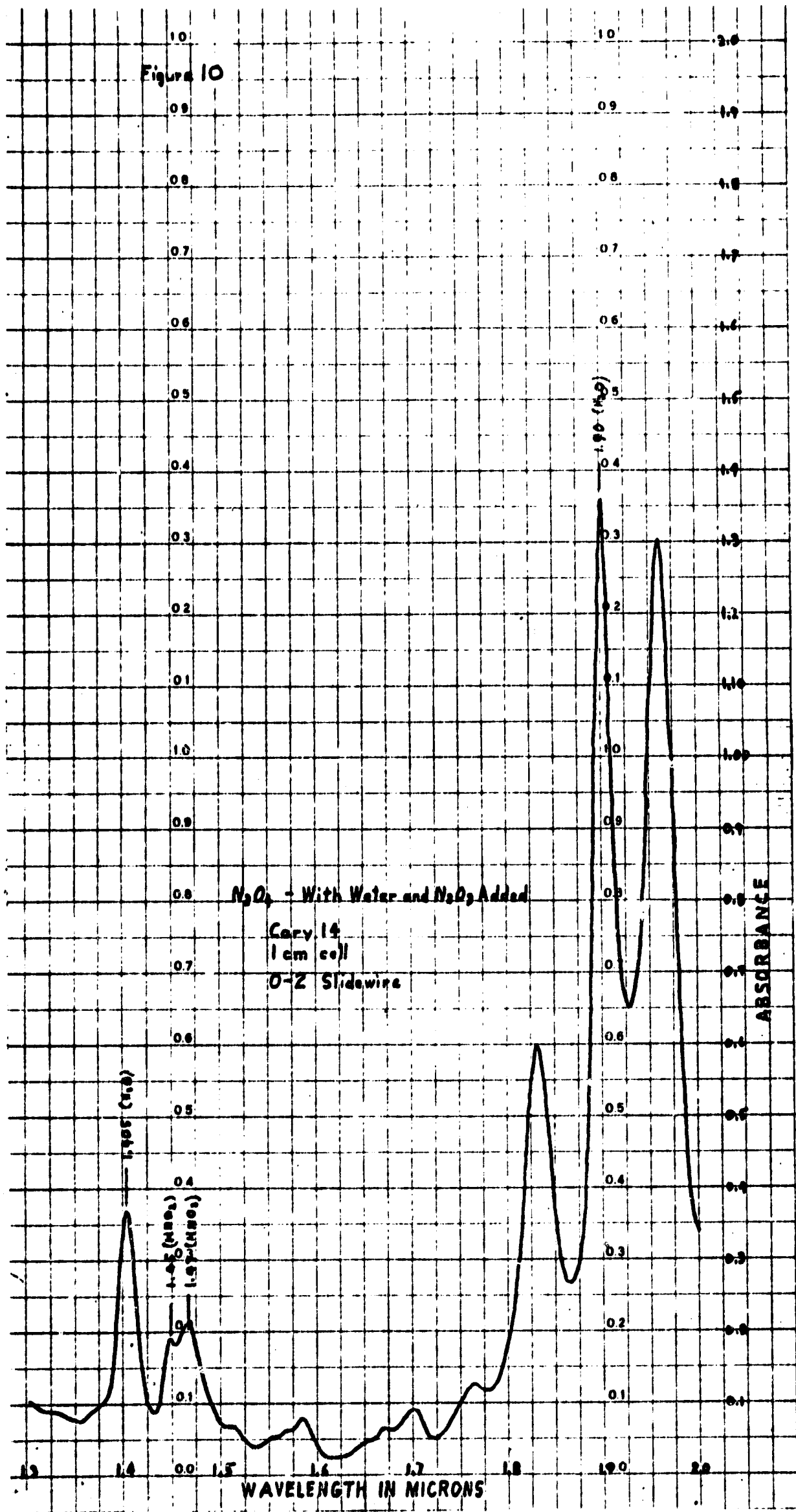


Figure 9

ABSORBANCE

Dry  $\text{CCl}_4 + \text{H}_2\text{O}_2$   
Cary 14  
10 cm cell  
0-0.2 Absorbance Slidewire

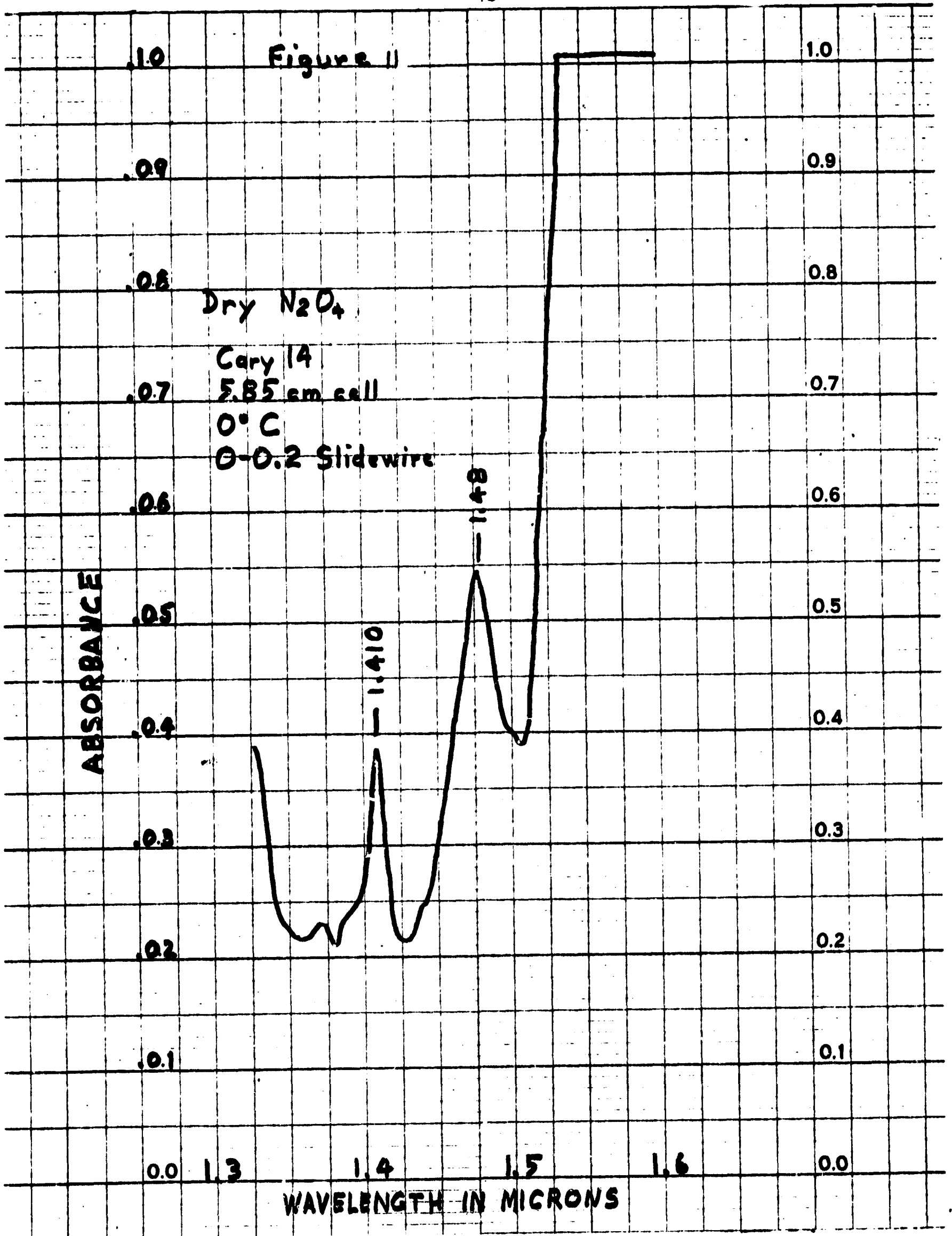




It has been noted that the ratio of the  $1.405\mu$  water band and the  $1.47\mu$   $\text{HNO}_3$  band in  $\text{N}_2\text{O}_4$  changes with temperature. This may prove valuable in studying the temperature dependence of the complicated equilibria involved. However, considerable further effort would be required for such studies and to calibrate the bands for quantitative measurement of the different species.

The resolution of the  $1.45\mu$  and  $1.47\mu$  bands is not very good and it may be necessary to resort to digitization and mathematical resolution of the peaks by computer, or to multicomponent spectrophotometric techniques.

Another complicating factor has been encountered in examining the spectra of "dehydrated" red  $\text{N}_2\text{O}_4$  at high sensitivity (5.85 cm. cell with 0-0.2 absorbance slidewire) for traces of residual protonated compounds. A pair of small bands at about  $1.41$  and  $1.48\mu$  are always present and constitute significant interferences in the quantitative measurement of very low levels of water and  $\text{HNO}_3$  (Figure 11). The intensities of these bands appear relatively constant for a given pathlength and are not temperature dependent nor affected by oxygen. They probably represent overtone or combination bands associated with  $\text{N}_2\text{O}_4$  itself. The band at  $1.48\mu$  interferes with the measurement of  $\text{HNO}_3$  at  $1.47\mu$  and may contribute a "blank" value equivalent to 100-200 ppm.  $\text{HNO}_3$ .



Until a suitable correction procedure can be worked out, all  $\text{HNO}_3$  analyses utilizing this procedure must be reported as maximum values.

All of the near-infrared work was performed on a Cary Model 14 spectrophotometer equipped with a 0-0.2 absorbance, scale expansion slidewire. The cells used were (1) the same temperature controlled cell used for the visible spectrophotometric determination of NO, with NIR-silica windows and a 1 cm. path-length, and (2) a special stainless steel, high pressure cell (Figure 12) having a 5.85 cm. pathlength and fitted with a tubular mixing chamber and a septum for the addition of various compounds.

Although various aspects of the NIR work require further study, it now appears that complete qualitative and quantitative characterization of the protonated species in liquid  $\text{N}_2\text{O}_4$  may be possible. A detailed description of the current version of the NIR procedure is included in the Appendix.

#### C. Dissolved Oxygen and Other Gases

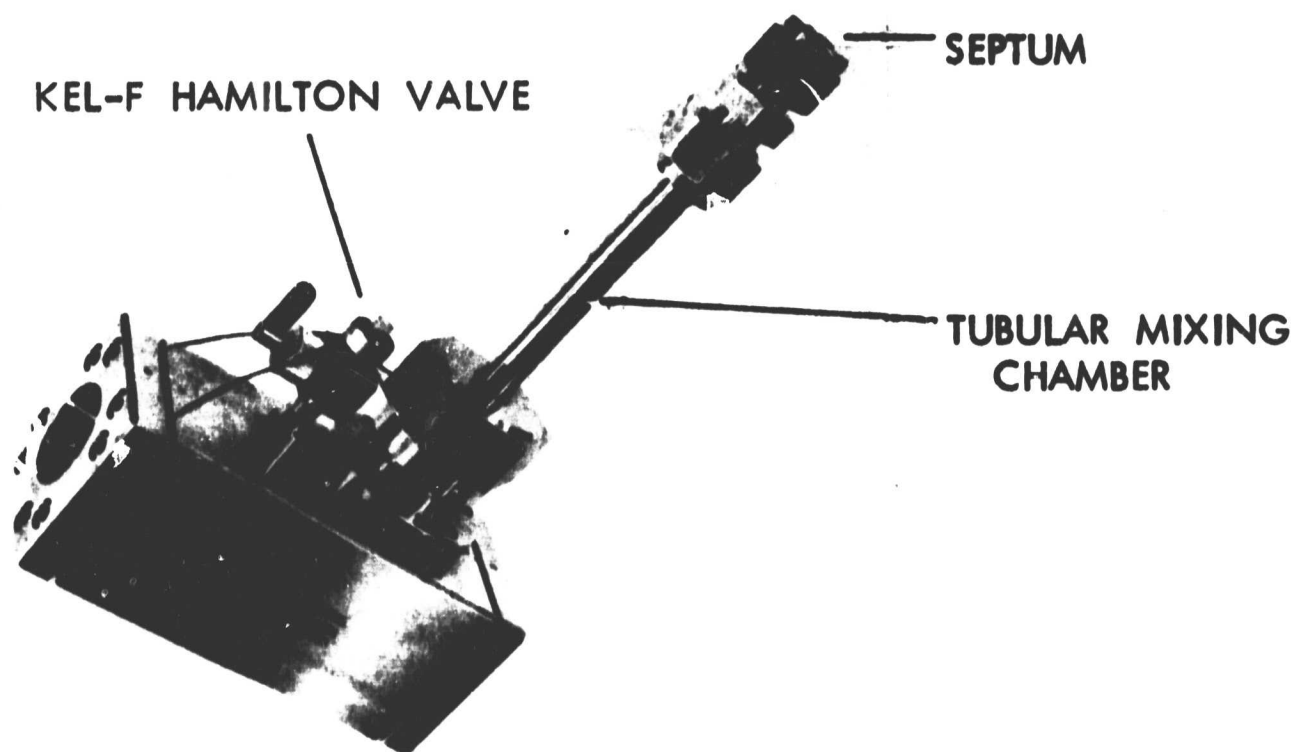
Liquid  $\text{N}_2\text{O}_4$  may be expected to contain small amounts of dissolved gases that have either been absorbed from the atmosphere or added during processing. Those most likely to be present are  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$  and A. In terms of possible influence on stress corrosion cracking,  $\text{O}_2$  is by far the most important. Thus, the majority of the analytical effort in this



-50-

FIGURE 12

SPECIAL STAINLESS STEEL CELL  
5.85 CM. PATHLENGTH NIR SILICA WINDOWS



area involved the investigation of methods for the quantitative determination of traces of dissolved  $O_2$  in liquid  $N_2O_4$ .

### 1. Mass Spectrometry

The first technique to be studied was mass spectrometry. Before any definitive quantitative work could be done, it was necessary to study the basic behavior of  $N_2O_4$  in the mass spectrometer. The primary objective of this work was to establish the amount of instrumental conditioning required to obtain a constant reference pattern for pure  $N_2O_4$  so that the contribution of minor impurities could be assessed. Two sampling techniques were also studied. These involved analysis of the head-space gases after several freeze-thaw cycles, and direct liquid sampling from a stainless steel, linear sampling valve.

Initial results showed that two 15-minute pressurizations with 100 microns of  $N_2O_4$  alternating with 15-minute evacuations were adequate to condition the system. The resulting mass patterns were quite reproducible and the principal ion intensities were found to be linear with respect to pressure. However, a number of difficulties were encountered:

a. Interference from  $^{14}N^{18}O^+$  ions and  $O_2$  formed by the thermal dissociation of  $NO_2$  yielded such a large peak at  $m/e = 32$  that small amounts of dissolved  $O_2$  (below about 50 ppm.) could not be determined with adequate sensitivity or precision.

b. The mass spectra consistently contained significant mass peaks not directly assignable to  $\text{N}_2\text{O}_4$ . These were finally attributed to reactions occurring with traces of nonvolatile organic residues in the mass spectrometer inlet and ion source. These reactions resulted in "apparent" concentrations of CO and  $\text{CO}_2$ . Although these peaks reached fairly constant levels after suitable conditioning, they also limited the sensitivity and precision of the method for traces of  $\text{CO}_2$  or CO.

c. Testing of freeze-thaw techniques to generate a gas phase suitable for analysis showed that it was very difficult to completely degas a sample of liquid  $\text{N}_2\text{O}_4$ . The direct injection of a liquid sample by means of a sample valve appeared preferable.

Because of the above and other minor problems, the mass spectrometry approach was abandoned in favor of gas chromatography.

## 2. Gas Chromatography

Previous work (4) on a gas chromatographic oxygen method has shown promise for development of a rapid and sensitive procedure. Since other workers (5) had indicated that NO could also be determined in gaseous systems containing  $\text{NO}_2$  and  $\text{O}_2$ , it was decided that an attempt to determine NO would also be made.

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(4) A. Z. Conner and G. A. Ward, Hercules Incorporated, report submitted to Bell Aerosystems Co., Feb. 11, 1966, Purchase Order 94835-39.

(5) J. M. Trowell, Anal. Chem., 37, 1152 (1965).

Initial work involved substitution of stainless steel tubing for the glass  $\text{N}_2\text{O}_4$  cold trap and an aluminum-Teflon valve for the three-way gas valve used to vent the trap. To evaluate the NO determination, a short precolumn of 0.5% Carbowax 1000 on glass beads was inserted before the cold trap, in an attempt to preseparate NO from the  $\text{N}_2\text{O}_4$  matrix (5). Preseparation is necessary since NO condenses with  $\text{NO}_2$  in the cold trap. It was found, however, that water adsorbed on the precolumn reacted with the  $\text{NO}_2$  to liberate NO. This, of course, provided erroneous results. Replacement of this packing with Poropak Q led to further problems since this material was nitrated by the  $\text{N}_2\text{O}_4$ , liberating interfering components. Hence, determination of NO by gas chromatography was abandoned.

Because of instrumental problems, the thermistor detector used in the original procedure was replaced by a hot wire detector. This rugged, stable detector was run at ambient temperature and a high filament current was used to provide a sensitivity equivalent to the thermistor detector.

In order to achieve a more flexible sampling arrangement, the liquid sampling valve was removed from the apparatus. Not only did the valve limit the sample size, but leakage problems were encountered. Further, it was felt that the large volume of liquid necessary to flush the valve might upset the oxygen equilibrium in the sample. Replacement was via a Swagelok "Tee" the center tap of which was fitted with

a silicone rubber septum. Attached to the center tap, and surrounding the septum, was a plastic glove bag which could be filled with an oxygen-free atmosphere (helium).

With the above arrangement, oxygen solubilities in acetone and carbon tetrachloride were determined and shown to be identical to those obtained with the liquid sampling valve. Comparison of oxygen solubilities in the literature (6) with the gas chromatographic values gave recoveries of 97.5 and 97.3% for acetone and carbon tetrachloride, respectively.

Initial analyses of  $N_2O_4$  samples indicated that the oxygen content might be low and near or below the 1 to 2 ppm. detection limit. Since the accuracy of measurements at this level is poor, and because lower oxygen levels might contribute significantly to the stress corrosion cracking mechanism, an improved procedure was sought.

Introduction on the market of a gas syringe, which is capable of isolating gas samples at pressures of up to 250 psi., and the appearance of a paper reporting the Henry's Law constants for gases dissolved in  $N_2O_4$  (7), suggested that an analysis of the gas phase over  $N_2O_4$  would lead to an indirect but sensitive method for oxygen in the liquid phase.

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(6) A. Seidell and W. F. Linke, "Solubilities of Inorganic and Metal Organic Compounds", Vol. II, 4th Edition, 1965, p. 1234.

(7) E. T. Chang and N. A. Gokcen, J. Phys. Chem., 70, 2394 (1966).

It was soon demonstrated that such an approach was feasible, and that the limit of detection would be near 10 ppb. using a 2.0 ml. gas sample. It was also shown that the gas phase analysis corresponded to results obtained by direct analysis of the liquid phase, at least over the range where oxygen could be accurately determined in the liquid (2 to 100 ppm.).

The glove bag arrangement provides an even more versatile sampling system than at first anticipated. Small sample bulbs can be placed entirely inside the bag's inert atmosphere (less than 30 ppm. of oxygen) and both liquid and gas phases can be analyzed if desired. Syringes can be used (the syringe must be cooled for the liquid phase analysis) which provides flexibility in sample size. Ports were also cut in the side of the bag so that a sample port arrangement attached to the stress corrosion cracking test cell could be isolated from the atmosphere. Samples of the cell content (gas or liquid phase) could be withdrawn and analyzed without fear of contamination from the atmosphere such as might be expected during transfer operations to a sample bulb.

The present procedure has been applied to a large number of samples during the past year. The method should be easily extended to the analysis of hydrogen and possibly other gaseous contaminants. The procedure is given in the Appendix.

#### D. Combined Chlorine

Any chlorine that may be present in  $N_2O_4$  is expected to be in the form of  $NOCl$ , although the presence of traces of inorganic chlorides is also possible. Since none of the available analytical methods for chloride appeared to have adequate specificity or sensitivity, a new approach was sought. Previous preliminary work had shown that a method based on x-ray fluorescence was promising. The method involves hydrolysis of an  $N_2O_4$  sample with aqueous  $AgNO_3$ , neutralization of the resulting aqueous solution with  $NH_4OH$ , reprecipitation of the  $AgCl$  with  $HNO_3$ , concentration of the  $AgCl$  on a Millipore filter, and specific determination of the chlorine content of the precipitate by x-ray fluorescence using the chlorine  $K\alpha$  line at  $4.73 \text{ \AA}$ . A General Electric Model XRD-6 spectrometer was used in this work.

Preliminary results obtained by this procedure showed that the method had adequate sensitivity but, based on the 95% confidence level of counting statistics, the expected level of precision was not obtained. The following procedural modifications were then made:

1. A 25 mm. Millipore filter was substituted for the original 47 mm. size.
2. Precipitation of the  $AgCl$  was carried out in dark flasks to minimize photo-decomposition of the precipitate.

3. The AgCl precipitate was cooled to 0°C. before filtering.

4. The precipitate was given a final wash with isopropanol to remove the AgCl that could not be washed from the sides of the filter holder with water.

The above modifications resulted in a procedure having very good precision and a 5-fold increase in sensitivity, i.e., from 5 counts per sec./ $\mu\text{g}$  Cl to 25 cps./ $\mu\text{g}$  Cl.

The precision of the overall method was established from replicate analyses of RR and G8  $\text{N}_2\text{O}_4$ . The combined chlorine content of RR  $\text{N}_2\text{O}_4$  was determined to be 15.9 ppm. with a relative standard deviation,  $S_r$ , of 4.7%. For G8  $\text{N}_2\text{O}_4$ , the chlorine content was 14.5 ppm. and  $S_r$  was 3.4%. A chloride standard yielding about the same number of counts as the  $\text{N}_2\text{O}_4$  samples could be analyzed with a relative standard deviation of 2.3%. The counting precision for the rotation mode was established by making five replicate counts on a typical sample. After each counting period the filter was removed and then reinstalled for the next count. The relative standard deviation was found to be 3.6%.

Based on a 7.5 g. sample and the  $K\alpha$  line of chlorine, 0.5 ppm. chlorine could easily be detected. This limit of detection could be reduced to 0.3 ppm. by use of the  $L\alpha$  line of silver, but specificity would be lost.

A detailed procedure for the x-ray fluorescence method is included in the Appendix.



#### E. Metallic Impurities

Nitrogen tetroxide contains very small amounts of metallic impurities that arise from contact with the plant materials of construction, principally stainless steel. Although it is highly unlikely that the presence of these metals contributes significantly to stress corrosion cracking, it was necessary to establish base compositions so that the amount of metals present after SCC tests could be determined. It was hoped that the amounts of metals dissolved during the tests might provide some clues to the SCC mechanism. Spectrochemical (emission spectrographic) and atomic absorption techniques were employed as the basic analysis methods. The former technique was used for preliminary screening analyses and the latter for final quantitative results. The principal metals monitored during SCC testing included Fe, Ti, Al, and V; atomic absorption methods for the determination of 16 other metals were also employed at different times. Several versions of standard visible spectrophotometric methods involving the use of orthophenanthroline and bathophenanthroline reagents for iron were also employed during this work.

A variety of sample preparation procedures were investigated in order to avoid the possible loss of relatively volatile metallic species, particularly iron compounds. These sample preparations included:

1. Controlled evaporation in a platinum dish followed by hydrolysis.

2. Controlled hydrolysis in an Erlenmeyer flask followed by evaporation in a platinum dish.

3. Hydrolysis in a closed system with off-gases vented through aqueous  $H_2O_2$  followed by evaporation in a platinum dish.

4. Hydrolysis in cold aqueous  $HCl$  followed by evaporation in a platinum dish.

5. Direct aspiration of cold  $N_2O_4$  into the atomic absorption atomizer chamber.

Determination of the metallic impurities in the starting materials, i.e., RR and G8  $N_2O_4$ , showed that the iron levels were 0.83 ppm. ( $S = 0.078$ ) in G8  $N_2O_4$  and 0.33 ppm. ( $S = 0.013$ ) in RR  $N_2O_4$  with virtually all other metals below 0.1 ppm.

Analyses performed before and after SCC testing showed that Fe, Al, and Na have less than 1 ppm. solubility in RR  $N_2O_4$  at room temperature. Titanium, under the same conditions, is considerably more soluble, i.e., up to 37 ppm. The solubility of vanadium is at least 9 ppm.

Nitrogen tetroxide containing approximately 0.8% NO may permit a slightly higher solubility of Fe, i.e., up to 1.6 ppm. Solubilities of other alloy constituents were below analytical detection limits.

The study involving 5 different sample preparation methods showed no significant differences in the amounts of determined iron. The controlled evaporation followed by hydrolysis was therefore selected as the method of choice. The presence of any significant amount of volatile iron compounds could not be demonstrated.

Pertinent procedures are included in the Appendix.

The analytical methods developed during its course of this work and described above are summarized in Table 2.

TABLE 2 - SUMMARY OF ANALYTICAL METHODS

1. Combined NO - Visible Spectrophotometry - 15 ppm. to 2%.
2. Total Protons - NMR - 0.03 to 0.5% as H<sub>2</sub>O, single scan  
0.01 to 0.03% as H<sub>2</sub>O, time-averaging
3. Distribution of Protonated Species - NIR - 200 to 10,000 ppm.  
HNO<sub>3</sub>  
Not yet calibrated for HNO<sub>2</sub>  
Not yet calibrated for H<sub>2</sub>O
4. Dissolved Oxygen - GC - 2 to 100 ppm. by liquid phase analysis  
<0.1 ppm. by gas phase analysis
5. Combined Chlorine - X-Ray Fluorescence - 1 to 100 ppm. Cl
6. Metallic Impurities - Atomic Absorption - <0.1 ppm. to 2 ppm.,  
20 different metals

#### V. Analysis of N<sub>2</sub>O<sub>4</sub> Samples

The original analytical data obtained by the Hercules plant laboratory on the cylinders of RR and G8 N<sub>2</sub>O<sub>4</sub> used in this program were reported in the Second Quarterly Report, HRC-67-3, p. 8. A summary of the analyses obtained on these same cylinders at the Hercules Research Center during the course of this work is given in Table 3. Higher results were obtained both for "water" content (0.09 vs. 0.05%) and chlorine content (28 ppm. vs. 10 ppm. as NOCl). However, the specification procedures for water and chlorine used by the plant are known to be deficient in several respects.

After the development and preliminary evaluation of the SCC test and the analytical methods, the following analysis scheme was used during the latter phases of the program:

##### 1. Before SCC Test

- a. Combined NO (Visible Spectrophotometry)
- b. Total protonated species (NMR)
- c. Dissolved O<sub>2</sub> (GC)

##### 2. After SCC Test

- a. Combined NO
- b. Total protonated species
- c. Dissolved O<sub>2</sub>
- d. Total chlorine (X-Ray Fluorescence)
- e. Dissolved metals: Ti, Al, V, Fe (Atomic Absorption)

The sampling procedures are described in detail in the Appendix.

TABLE 3 - ANALYSIS OF PLANT  $N_2O_4$  FOR PROGRAM USE

Sample	RR (Cylinder 127)	G8 (Cylinder No. 120)
Combined NO, wt.%	-	0.72
Total protons as $H_2O$ , wt.%	0.088 (Av. 4 detn.)	0.090 (Av. 4 detn.)
Total chlorine, ppm.	15.9 (Av. 5 detn.)	14.5 (Av. 5 detn.)
Metals, ppm.		
Fe	0.31	0.83
Al	<0.5	<0.5
Ti	<0.7	<0.7
V	<0.1	<0.1
Cr	<0.03	<0.03
Na	<0.05	<0.05
K	<0.05	<0.05
Zn	<0.05	<0.05
Ca	0.006	0.02
Pb	<0.1	<0.1
Ni	<0.03	<0.03
Mg	<0.06	<0.06
Mn	<0.05	<0.05
Si	0.1	0.1
Cu	<0.01	<0.01
Ag	<0.006	<0.006
Sn	<0.02	<0.02
Bi	<0.1	<0.1
Sb	<0.1	<0.1
Cd	<0.1	<0.1
B	<0.1	<0.1
Co	<0.1	<0.1

## DISCUSSION OF RESULTS

During the course of this work, approximately 25 SCC test runs were made. As previously discussed, a number of these runs were orienting experiments performed during the early stages of test development and were used to assess the effects of U-bend specimen parameters (bend orientations, stress levels, etc.) and other test variables. The remainder of the tests (with a few exceptions) were run under standard conditions after the composition of the  $N_2O_4$  had been adjusted and established by analysis. Standard test conditions involved the immersion of 10 stressed U-bend specimens in liquid  $N_2O_4$  for approximately 72 hours at 165°F. (74°C.) The principal experimental observations from the above tests are discussed below.

### I. Basic Types of $N_2O_4$ - SCC Testing

The results obtained by applying the standard SCC test to the basic types of  $N_2O_4$  involved in this program are summarized in Table 4 and discussed below.

Typical "red"  $N_2O_4$  (M11-P-26539A), as received from the production plant, caused cracking in all U-bend specimens tested (ca. 70) after 24-72 hour exposures. It was classified as Red Reactive (RR)  $N_2O_4$ .

As expected, "green"  $N_2O_4$  (G8) containing 0.7-0.8% combined NO (MSC-PPD-2A) produced no cracks in any of the specimens tested. Identical behavior was observed when the

TABLE 4 - SCC TESTING OF 6Al4V ELI TITANIUM ALLOY IN BASIC TYPES OF N<sub>2</sub>O<sub>4</sub>

N <sub>2</sub> O <sub>4</sub> Type	Test Parameter		Failure Rate
Reactive N <sub>2</sub> O <sub>4</sub> Mil-P-265359B	Time	24 Hrs. at 162°F.	10/10
	Temp.	70-80°F. <76 Hrs.	10/10
	Stress Level	30% of Yield Strength	2/2
		Residual Shearing Stress	2/2
		U-Bend Forming Stress	8/8
Green N <sub>2</sub> O <sub>4</sub> MSC-PPD-2A		Identification Stamps	70/70
	Compon Orientation (Isotropy)	Parallel To Rolling Direction	10/10
		Transverse To Rolling Direction	10/10
	NO Concentration	7200 ppm.	0/20
		4000 ppm.	0/10
Red Nonreactive N <sub>2</sub> O <sub>4</sub>	NO Concentration	500 ppm.	0/10

Notes:

- Parameter Range for Standard Tests
 

Time	72 ± 12 Hours
Temp.	165 ± 3°F.
Stress Level	90% of yield strength; longitudinal YS 136,900 psi. transverse YS 139,100 psi.
Specimen	
Shape	U-bend formed from 3/4 x 5 x 1/16-inch strip.
Bend Radius	5t
- Failure Rate of 0/10 indicates no cracks detected in 10 exposed specimens examined at 400X.

G8  $N_2O_4$  was diluted with RR  $N_2O_4$  to produce material containing 0.4% NO. A total of about 30 U-bend specimens were exposed to the above two types of  $N_2O_4$ , without any trace of cracking.

Red Nonreactive (RN)  $N_2O_4$  is defined in this program as material that is visually indistinguishable from RR  $N_2O_4$  at 0°C. and which does not cause SCC in the standard test. Samples of RR  $N_2O_4$  having a normal "water" content, i.e. 0.08-0.09%, and to which 150-600 ppm. NO was added, fit the definition. A similar sample to which only 35-45 ppm. NO was added cracked all test specimens. As much as 800 ppm. of NO can be added to RR  $N_2O_4$  before a green cast can be observed visually at 0°C. A different type of RN  $N_2O_4$  will be discussed in a separate section below.

## II. Effect of Compositional Factors on SCC

Experiments were performed in an attempt to establish the effects of dissolved oxygen, protumted species, and NO levels on SCC. The results are summarized in Table 5 and Figure 13, and are discussed below.

In a limited series of tests, samples of RR  $N_2O_4$  containing <1 to 20 ppm. dissolved  $O_2$  caused cracking in test specimens at the normal test temperature of 165°F. However, two 76-hour runs at 70°-80°F. showed that a RR  $N_2O_4$  sample containing about 20 ppm.  $O_2$  caused 50-100 times more cracking (100-800 cracks/cm.<sup>2</sup>) than a sample whose  $O_2$  content had been reduced to about 1 ppm. (2-8 cracks/cm.<sup>2</sup>). Because



TABLE 5 - RR N2O4 MODIFICATIONS & SCC OF 6Al4V ELI TITANIUM ALLOY

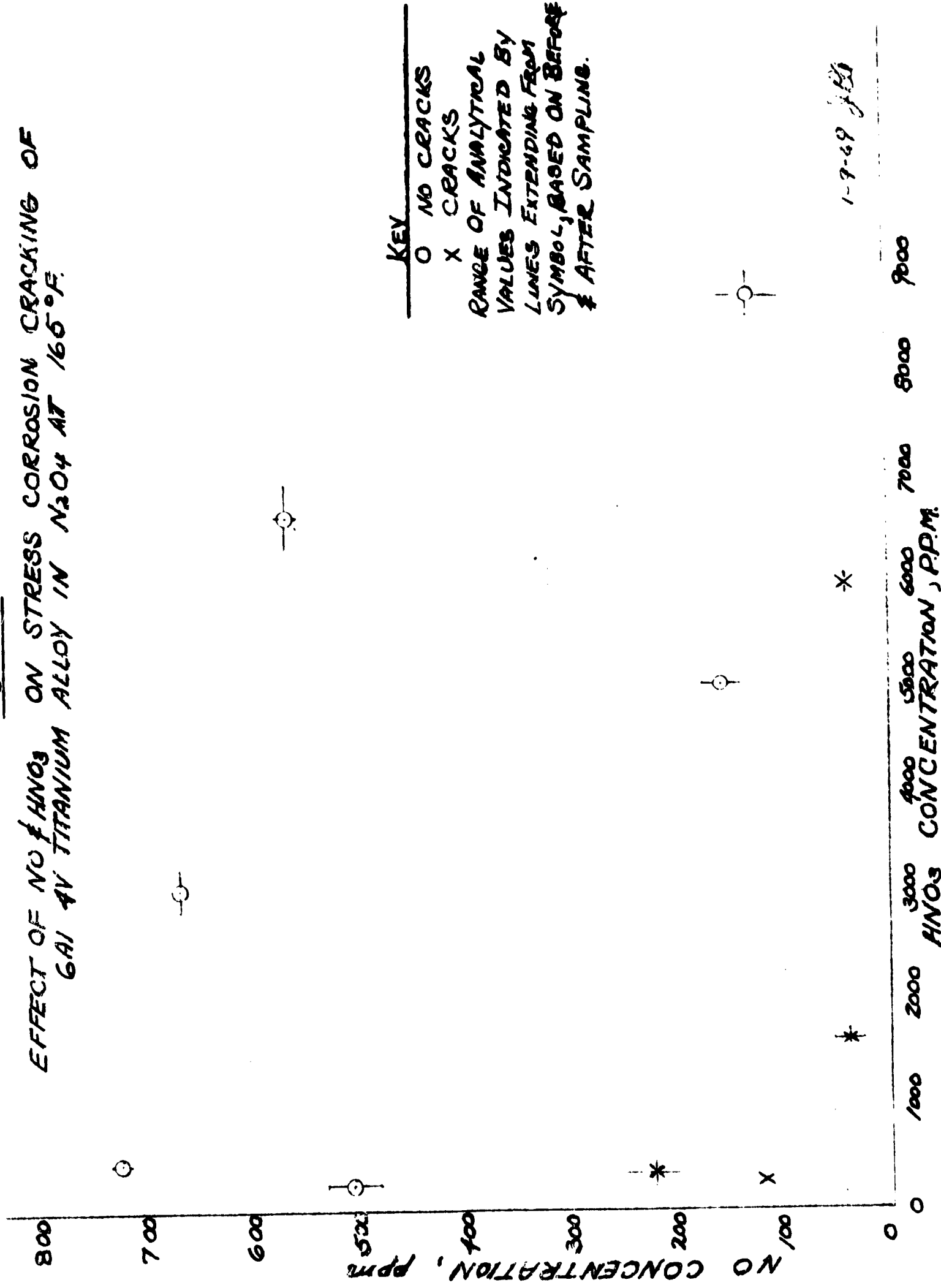
Run No.	Modification	Test Condition			Failure Rate
		O <sub>2</sub> , ppm.	Temp., °F.		
11	None	10-20	70-80	10/10	(NCD) <sup>2</sup>
10	Deoxygenation	1	70-80	10/10	(ACD) <sup>3</sup>
14		0.2	165	10/10	(NCD)
15	Dehydration (Deprotonation)	120	245	10/10	(NCD)
21		255	270	10/10	(NCD)
19	+N <sub>2</sub>	535	285	0/10	
20		740	420	0/10	
17	+99+% HNO <sub>3</sub>	26	1680	10/10	(NCD)
18	+H <sub>2</sub> O	675	3000	0/10	
25	Normal +NO	175	5000	0/10	
24	Normal +H <sub>2</sub> O + O <sub>2</sub>	160	8500	0/10	
23	Normal +H <sub>2</sub> O	580	6900	0/10	

Notes:

1. Failure Rate = number failed/number exposed.
2. NCD = normal crack density 100-800 cracks/cm.<sup>2</sup>
3. ACD = abnormal crack density 2-8 cracks/cm.<sup>2</sup>

Figure 13

EFFECT OF NO<sub>2</sub> & HNO<sub>3</sub> ON STRESS CORROSION CRACKING OF  
GALV TITANIUM ALLOY IN NaOH AT 165°F.



of the very limited data these results can not be considered definitive but only indicative of a possibly critical oxygen effect.

Attempts to "dry" or "dehydrate"  $\text{N}_2\text{O}_4$  were made prior to the discovery of an analytical method capable of establishing the distribution of protonated species in liquid  $\text{N}_2\text{O}_4$ . These "dehydration" experiments were monitored by NMR which only measures total proton level without indicating the nature of the protonated species. Passage of  $\text{N}_2\text{O}_4$  vapors through a bed of Type 3A Molecular Sieve usually reduced the proton level by a factor of about 20 and also produced a small amount of NO in the final product.

A typical RR  $\text{N}_2\text{O}_4$  having a proton content of 0.08-0.09% as  $\text{H}_2\text{O}$  (5600-6300 ppm. as  $\text{HNO}_3$ ) was usually converted into  $\text{N}_2\text{O}_4$  containing 250-350 ppm.  $\text{HNO}_3$  and 120-250 ppm. combined NO. This material cracked all specimens in the standard SCC test. Complete inhibition of cracking was only obtained in "dehydrated" samples when the NO level was raised to above 500 ppm. In typical RR  $\text{N}_2\text{O}_4$  the presence of as little as 150 ppm. combined NO is sufficient to inhibit SCC. These results thus demonstrated the existence of a definite interdependency between combined NO and protonated species concentrations with regard to SCC behavior.

Several other miscellaneous experiments are described in Table 5. A sample of "dehydrated" RR  $\text{N}_2\text{O}_4$  with a low NO content (25-50 ppm.) was mixed with a small amount of 99%  $\text{HNO}_3$  (ca. 1600 ppm.). The resulting mixture cracked 10/10 U-bend specimens. The addition of water to a "dehydrated" RR  $\text{N}_2\text{O}_4$  sample resulted in a material containing 670 ppm. combined NO and 460 ppm. " $\text{H}_2\text{O}$ " calculated from the total proton content. No cracking occurred in any of the 10 specimens exposed to this sample in a standard test.

The development of an analytical method capable of establishing the distribution of protonated species in liquid  $\text{N}_2\text{O}_4$  samples was accomplished late in the program. Unfortunately, it was not available for use in conjunction with most of the test mixtures described above. However, as previously described in Section 4B, sufficient work was done to establish that oxygen-treated  $\text{N}_2\text{O}_4$  contains protons only in the form of  $\text{HNO}_3$ . Nonoxygenated samples may contain varying ratios of three different protonated species, i.e.  $\text{HNO}_3$ ,  $\text{HNO}_2$ , and  $\text{H}_2\text{O}$ .

During the course of the SCC testing program, the analytical data suggested that the combined NO content of a given sample decreased slightly during an SCC run, and the combined chlorine content did not change. The data were inadequate for unequivocal proof of these apparent observations.

### III. Determination of Corrosion Rates

The standard gravimetric technique of weight loss per unit area for the time of the experiment was used for corrosion rate determinations. Either U-bends or milled U-bend blanks were used. A summary of corrosion rate determinations appear in Table 6A.

### IV. Metal Solubility in N<sub>2</sub>O<sub>4</sub>

Iron was the most prominent metal found in N<sub>2</sub>O<sub>4</sub> sampled directly from the steel storage cylinders. More was found in G8 N<sub>2</sub>O<sub>4</sub> (1.1 ppm.), than in RR N<sub>2</sub>O<sub>4</sub> (0.30-0.4 ppm.). This difference may be due to soluble complex formation with nitric oxide to form Fe (NO)<sub>n</sub> (NO<sub>3</sub>)<sub>x</sub>. Thus, G8 with 7200 ppm. NO might be expected to contain more Fe in solution than RR without NO. Nothing is known of the amount of insoluble iron present in these containers resulting from corrosion reactions.

The corrosion of titanium alloy coupons introduced metals into solution in proportion to corrosion rate but not in proportion to alloy composition. Essentially no detectable increase in Ti, Al or V was found in noncorrosive G8 N<sub>2</sub>O<sub>4</sub> after exposure of 10 specimens for 68 hours at 165°F. On the other hand, RR N<sub>2</sub>O<sub>4</sub> in contact with coupons under similar conditions, was found to contain 10-37 ppm. Ti, 0.4-0.9 ppm. Al, and 2-9 ppm. V. Directly from the storage cylinders, both N<sub>2</sub>O<sub>4</sub> types contain <0.65 ppm. Ti, <0.4 ppm. Al, and <0.13 ppm. V. Aluminum is less soluble than either Ti or V, definitely

TABLE 6A - CORROSION OF 6Al4V ELI TITANIUM ALLOY BY N<sub>2</sub>O<sub>4</sub>

N <sub>2</sub> O <sub>4</sub> Type	Exp. Time Hours	Temp. °F.	Corrosion Rate, mils/yr.	Remarks
Red Reactive (RR) Deoxygenated	76	70-80	Not detected, <0.06	Mill-P-26539B
RR	24	162	0.9 <sup>+0.3</sup> -0.2	Mill-P-26539B
	69.2	165	0.8 ±0.1	Mill-P-26539B
Green (G8), 0.8% NO	70	166	Not detected, <0.06	MSC-PPD-2A
G4, 0.4% NO	69	165	Not detected, <0.06	Blend of RR & G8
Red Nonreactive (RN), 0.05% NO	70	165	0.14 <sup>+0.09</sup> -0.05	Blend of RR & G8

not in relationship to its concentration in the alloy. It was found in solids precipitated from solution more nearly in proportion to its alloy concentration whereas vanadium was not. Pertinent data are compiled in Table 6B.

V. Analysis of MSFC Sample of RN N<sub>2</sub>O<sub>4</sub>

Two No. 4 cylinders of N<sub>2</sub>O<sub>4</sub> from the Marshall Space Flight Center were received for analytical characterization. They supposedly represented a single sample of a red-nonreactive (RN) N<sub>2</sub>O<sub>4</sub>. They were arbitrarily designated cylinders A and B.

The samples were analyzed for dissolved oxygen, combined NO, protonated species, metals, and chlorine by the methods developed under this contract. A standard stress corrosion cracking test also was performed using 10 prestressed 6Al4V ELI titanium alloy U-bend specimens. Since some of the N<sub>2</sub>O<sub>4</sub> had been used for analysis prior to the SCC test, the test cell was filled with a composite of both sample cylinders. It is estimated that about 1/4 of the N<sub>2</sub>O<sub>4</sub> came from one cylinder (A) and 3/4 from the second (B).

In addition, a sample was taken during preparation of the SCC test cell and analyzed for O<sub>2</sub> and NO. This sample consisted of about 100 ml. of liquid N<sub>2</sub>O<sub>4</sub> that was bled from the SCC cell after filling in order to provide expansion volume. The contents of the SCC cell were also analyzed upon termination of the oven exposure.

TABLE 68 - QUANTITY OF TRACE ELEMENTS IN  $N_2O_4$  BEFORE AND AFTER STRESS CORROSION CRACKING TESTS

(Concentration, ppm.)																			
N <sub>2</sub> O <sub>4</sub> Type	Run No.	RR Cylinder <sup>2</sup> Supply	GS Cylinder <sup>2</sup> Supply	RR 1-23	GS 23	RR 3	GS 5	RR 6	G4	RR		Deoxygenated RR	Deoxygenated With GS	Dry RR + 99% HNO <sub>3</sub>	Dried RR + H <sub>2</sub> C	Dry RR + NC	Dry RR + NO	Dry RR	
										Before	After								
										Before	After								
Element																			
Fe		0.33	1.1	1.3	1.6	0.63	0.97	0.28	0.49	0.66	0.35	0.46	0.32	0.47	0.05	0.09	0.04	0.14	0.24
Ti		<0.65	<0.65	25.5	<0.65	25.	<1.	31.	<0.7	<0.7	<0.8	<0.8	10.	36.9	2.6	<0.2	<0.4	<0.4	0.5
Al		<0.33	<0.33	0.42	<0.33	0.7	<0.5	0.9	<0.4	<0.4	<0.4	<0.4	<0.2	0.89	<0.5	<0.5	<0.2	<0.2	<0.2
V		<0.13	<0.13	9.0	<0.13	6.4	<0.3	6.2	<0.07	<0.07	<0.1	<0.1	4.5	6.9	0.51	<0.1	<0.1	<0.1	0.44
Cr		<0.03	<0.03	<0.03	<0.03														
Ni		<0.03	<0.03	<0.03	<0.03														
Cl						16.0							13.0	15.9	15.6				
SCC Failure Rate	-	-	-	10/10	0/10	10/10	0/10	10/10	0/10	0/10	0/10	0/10	10/10	10/10	10/10	0/10	0/10	0/10	10/10
NO Conc., ppm.	0	7200	7200	0	7200	0	7200	0	4000	500	500	500	Nil	0	44	675	535	740	255

Notes: 1.  $N_2O_4$  Type:

RR = Red Reactive Mil-P-265398  
GS = Green 0.8% NO MSC-PPD-2A  
G4 = Green 0.4% NO

2. Sampling Date: Cylinder 12-13-67 (Filled 9-8-67) Test Cell 5-23-68

3. Stainless steel end plates used for test cell in these runs.



During this work, it was noted that the samples contained substantially more fine particulate matter than the  $N_2O_4$  taken from the 1-ton cylinders used in the contract work. In addition, during the evaporation and hydrolysis of samples from Cylinder B for metals analysis, a significant amount of a water-insoluble scum was observed. This contaminant was soluble in methylene chloride and acetone and was qualitatively examined by infrared and NMR spectroscopy. Cylinder A was emptied into the test cell prior to this observation so it is not known whether it also contained this contaminant.

The analytical results are compiled in Table 7. The SCC test (72 hours at 165°F.) resulted in one cracked U-bend and 9 uncracked. The latter 9 specimens showed no microscopic indications of attack.

The infrared spectrum of the water-insoluble scum from Cylinder B was studied. It was obtained from a film cast from  $CH_2Cl_2$  solution on a salt plate. Its pertinent features were aliphatic C-H bands at 2800-3000  $cm^{-1}$ , carboxylic acid and probably carboxylic salt bands at 1730 and 1550  $cm^{-1}$ , and what are probably nitrate ester bands at 1640, 1280, and 860  $cm^{-1}$ . The presence of nitrogen in the residue (3.6%) was confirmed by elemental analysis. The metal content of the residue was found to be very low (emission spectroscopy).

NMR spectra of the residue also were obtained. Only a portion of the sample was soluble in  $CDCl_3$  while the remainder

TABLE 7 - ANALYSIS OF NASA RN  $N_2O_4$  SAMPLES

	A	B	Test Cell	
			Before SCC Test	After SCC Test
Dissolved $O_2$ , ppm.(a)				
Liquid Phase Analysis	1.2	1.2	2.2	Not detected
Calc. from Gas Phase Analysis	11.8	9.8	1.8	0.05
Combined NO, ppm.	~10	~10	<5	40 ± 15
Protonated Species, ppm.(b)				
$HNO_3$	6200	6200	-	6450
$HNO_2$	N.D.	N.D.	-	N.D.
$H_2O$	N.D.	N.D.	-	N.D.
Combined Cl, ppm.	-	<0.5	-	0.8
Metallic Impurities, ppm.				
Fe	-	2.7	0.66	1.0
Na	-	0.6	0.08	0.08
Cu	-	0.06	0.016	0.04
Cr	-	0.16	0.14	0.06
Ni	-	0.15	0.07	0.05
Mn	-	0.04	0.24	0.008
Mg	-	0.02	-	0.02
Ca	-	0.08	0.03	0.03
Zn	-	1.9	0.7	0.19
Pb	-	1.2	0.24	<0.1
Ti	-	<1.2	-	<1.2
Al	-	<0.6	-	<0.6
V	-	<0.12	-	<0.12

Notes: (a) All results are average of 2-9 determinations. Evidence for the presence of dissolved  $N_2$  and CO in all samples.

(b) Determined by near IR. Cylinder B was also analyzed for total proton content by NMR: 6930 ppm. as  $HNO_3$ .

dissolved in deuteroacetone. The spectra provided little additional information. The presence of methylene protons was confirmed in the  $\text{CDCl}_3$  soluble fraction and little else was seen because of the limited sample size. An unidentified band in the deuteroacetone soluble fraction may have been due to protons near nitro groups or to salt formation. Protons from the  $\text{CH}_3\text{O-Si}$  grouping were looked for but not found.

A considerable amount of the above data indicates that this is definitely an atypical sample of  $\text{N}_2\text{O}_4$ :

1. Unusual amount of particulate matter; also indicated by high metals content of Cylinder B.
2. Contamination by significant amount of organic matter.
3. Unusually low combined Cl content.
4. Unusual lack of agreement between liquid and gas phase determination of  $\text{O}_2$  in cylinder samples.
5. Very low observed  $\text{O}_2$  level after SCC test.
6. Evidence for presence of CO in all samples.

On the basis of the usual analyses, it would be predicted that the sample would crack all 10 U-bends in the SCC test. Only one cracked and the others were unaffected. This is the only sample that has yielded equivocal results in the standard SCC test.

The most reasonable conclusion is that the presence of the organic matter creates an inhibiting action in the SCC test. Two possible modes of action can be postulated. First,

the organic matter is more susceptible to oxidative attack than the alloy and is, in effect, acting as an antioxidant.

Secondly, the organic molecules containing carboxyl groups could be adsorbed on the metal surface and thus provide a protective barrier against attack. The low  $O_2$  content after SCC test, the presence of dissolved CO, and the apparent increase in NO content after the SCC test, tend to confirm this general hypothesis. No explanation for the one cracked U-bend can be offered.

### CONCLUSIONS

The majority of the specific experimental goals of this program have been achieved.

(1) A satisfactory stress corrosion cracking test that conforms to the original requirements of the program was developed. As applied to the alloy and  $N_2O_4$  samples used in this work, extremely consistent test results were obtained.

(2) Six new analytical methods were developed that are capable of detecting and determining significant differences in the minor component composition of different types of  $N_2O_4$ . For the first time, it is now possible to determine combined NO content down to 15 ppm., dissolved  $O_2$  content down to <0.1 ppm., and the amount and distribution of the protonated species in liquid  $N_2O_4$ .

(3) Techniques were developed for the quantitative adjustment of the minor constituent composition of  $N_2O_4$  systems, including a procedure for substantially reducing the level of protonated species.

(4) The above methods and techniques were successfully employed in the preparation, analysis, and SCC testing of about 25 varied  $N_2O_4$  compositions in attempting to correlate composition with SCC behavior.

The data and knowledge obtained from the above experimental program have been sufficient to establish the SCC test behavior of 6Al 4V ELI titanium alloy in the commonly encountered commercial type of  $N_2O_4$ . Correlation of combined NO-protonated

species concentrations with SCC test behavior was partially achieved in terms of critical concentration levels. It is believed that the SCC test behavior of a large percentage of  $N_2O_4$  systems can accurately be predicted from composition information. However, when the basic  $N_2O_4$  equilibrium system is contaminated with extraneous organic or inorganic compounds, SCC behavior cannot be predicted.

It has been shown that stress corrosion cracking behavior can be drastically influenced by very minor changes in composition produced by constituent addition or by shifting equilibria. Typical oxygenated  $N_2O_4$  containing  $HNO_3$  attacks 6Al 4V ELI titanium alloy to a small but measurable degree. This attack leads to cracking under conditions of stress. The presence of as little as 150 ppm. combined NO effectively stops both cracking and ordinary corrosion. However, if the proton level of the  $N_2O_4$  is decreased, more NO is required to halt the attack. This points to the presence of  $HNO_2$  and/or  $H_2O$ , rather than  $N_2O_3$ , as the main critical indicators of a nonreactive system. The nature of the inhibitory process is still in doubt. An inhibiting species may react with active surfaces to prevent further attack or it may prevent the formation of an attacking species.

The available evidence, most of which is circumstantial, appears to favor the hypothesis of an oxidative attack mechanism, although the specific nature of the attacking species is still unknown. The complexity of this and associated problems clearly indicate the need for additional experimental investigation.

### RECOMMENDATIONS FOR FUTURE WORK

Further experimental work is needed in order to more accurately define the  $\text{N}_2\text{O}_4$  equilibrium system and to establish its relationship to the stress corrosion cracking of titanium alloys. The roles of key impurities such as  $\text{O}_2$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ , and  $\text{H}_2\text{O}$  require further elucidation, and critical concentrations should be more clearly established.

It is recommended that the following experimentation be considered in any future work:

(1) Design and construction of an improved apparatus for the production of substantial amounts of  $\text{N}_2\text{O}_4$  containing less than 50 ppm. of protonated species.

(2) Design and construction of an improved system for the precise and accurate addition of known amounts of compounds to dehydrated  $\text{N}_2\text{O}_4$  in amounts down to 25 ppm.

(3) A study by near-infrared spectroscopy of the distribution of protonated species in  $\text{N}_2\text{O}_4$  as related to composition and temperature of the  $\text{N}_2\text{O}_4$ - $\text{N}_2\text{O}_3$ - $\text{H}_2\text{O}$  system.

(4) A study by ultraviolet spectroscopy, and possibly other techniques, of the  $\text{NO}_2 \rightleftharpoons \text{NO} + \text{O}_2$  equilibrium in one-phase, and possibly two-phase,  $\text{N}_2\text{O}_4$  systems in the temperature range of 60-75°C.

(5) A study of the dependence of the stress corrosion cracking reaction of  $\text{N}_2\text{O}_4$  with 6Al 4V titanium alloy as a function of temperature and oxygen content.

(6) A more precise correlation study of composition with

stress corrosion cracking in the critical concentration ranges approximately established by this program.

(7) A study of the effect of the addition of organic compounds (hydrocarbon, fluorocarbon oils, acids, antioxidants) on SCC.

Many of the experimental aspects of the program described above are difficult and the complexity of the equilibria involved in nitrogen oxide systems is formidable. However, the successful accomplishment of the majority of the objectives of Contract NAS8-21207, plus the increased capabilities and experience acquired during the past year, indicate a good probability of major goal achievement in this proposed program.



## APPENDIX

### I

#### A. Phase A - Development of Standard SCC Test

##### 1. Test Specimen Preparations; U-Bends

###### a. Material

Mill annealed 6 Al 4 V ELI titanium alloy sheet with known physical properties and chemical analysis is used for the preparation of U-bends. The sheet should pass the 4t bend test, be between 1/16 and 3/32-inch thick, have the rolling direction indicated and possess 240 grit ground surfaces. Surfaces should be protected by paper to limit marring during subsequent handling.

###### b. Prebend Blanks

In this work processing was done on available universal Sheet Metal and Machine Shop equipment. Processing was in batches of 50 to 100 specimens through the drilling operation. Batch processing was employed because all of the equipment surfaces, potentially in contact with the specimens or machining coolant, were decontaminated (oil, grease and cutting oils removed) and washed or wiped with acetone. The coolant, 5% aqueous sodium nitrite by weight (AR grade in distilled water), was applied from a portable reservoir-recirculating system to eliminate the chore of decontaminating integral cooling systems. The cleanliness precautions used may have been exaggerated and the limits of cleanliness should be explored in future work. Prebend blanks were prepared as indicated below.

(1) Shearing

Power shear a suitable number of 1-inch wide blanks from a 5-1/4-inch strip of the test metal. The strip can be purchased in this width or be sheared from a larger stock sheet.

(2) Milling

Install 10 specimens in a milling jig (Figure 14) with protective paper intact. Back the first and last specimen with 1x5x1/32-inch soft aluminum sheet. Place a 1x5x1/6-inch hot rolled steel throwaway plate against one face of the stack then advance cap screws against the steel plate to lock specimen blanks in place. Adjust 5% aqueous sodium nitrite coolant flow and climb mill 1/8-inch off the long and short dimension. Cutter speed, 41 surface feet/min.; feed, 2.3 inch/min.; chip load, 0.002 inch. Remove stack of blanks and rotate in jig. Finish milling the remaining two edges to the final blank dimension of  $0.750 \pm 0.002 \times 5.000 \pm 0.002$  inch.

(3) Drilling

The group of ten blanks from the milling operation with aluminum protectors and steel throwaway plate are transferred to a drilling jig (Figure 15). Another steel plate is added to protect the newly milled edges and to distribute the load from the locking screws. With adequate coolant flow, a 9/32-inch hole is drilled through the blanks, aluminum protector and steel throwaway plate. Pin stops in the jig are used to properly locate the blanks beneath the drilling bushings. Drill holes at 310 rpm. with 0.004 inch feed/rev. and a 0.002-inch chip load. After both holes

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FIGURE 14  
MILLING JIG - SCC BLANKS

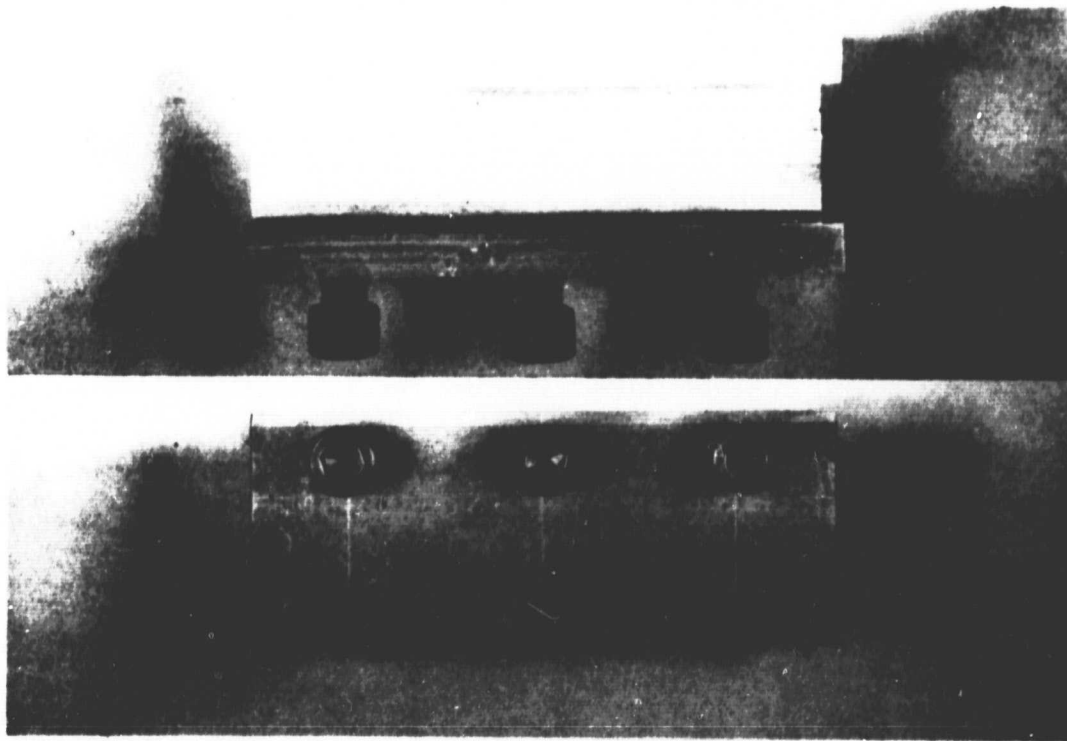
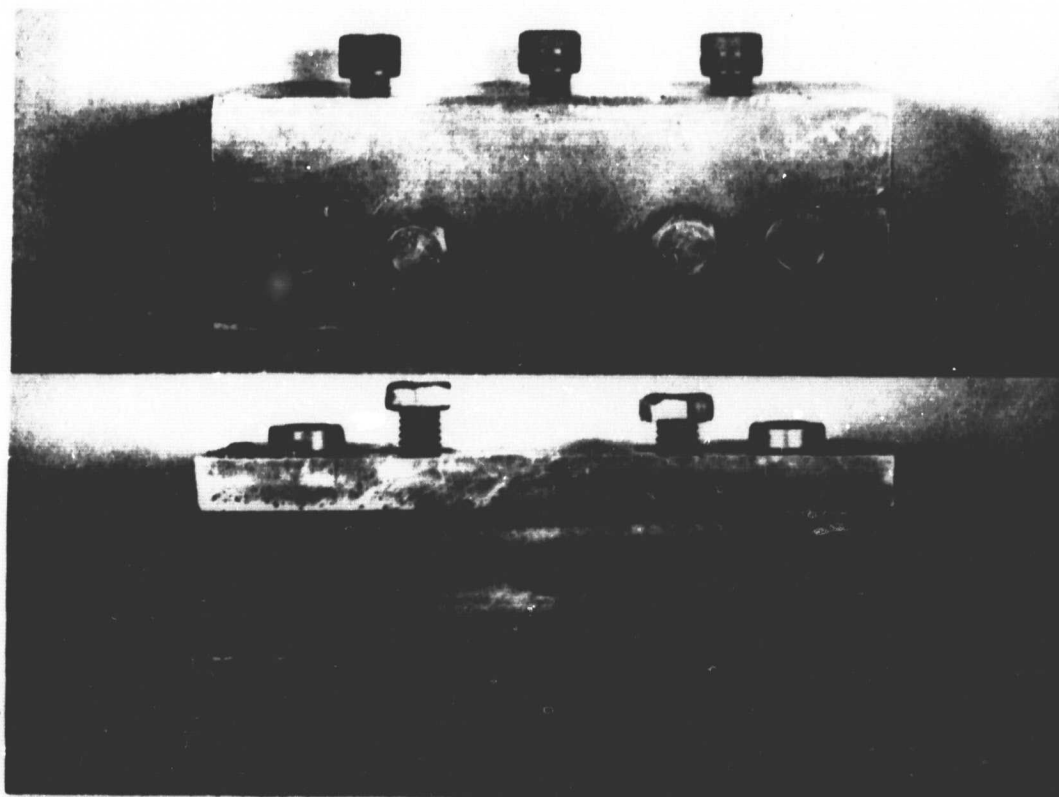


FIGURE 15  
DRILLING JIG - SCC BLANKS



SCALE = 1/2 SIZE

are drilled, remove the blanks from the jig, separate, remove the protective paper, then dry each blank with paper toweling. If processing is to continue, place the blanks on clean paper (do not stack or mar surfaces). Protect each blank with a glassine envelope, if operations are to be performed at a later time.

(4) Deburring

Deburr all edges dry and by hand with 400 grit silicon carbide paper. Remove the burr from the hole edges with a 9/32-inch hand counterbore tool. Place each deburred blank in its protective glassine envelope.

c. U-Prebends

(1) Bending

All bending was carried out on a Model No. 2 Di-Acro Bender modified to accept a special clamping device and a nosepiece roller (Figure 16). Preliminary adjustment of stops, bend angle, etc., are made with cold rolled steel sheared blanks of the same dimensions as the titanium blanks. Additional adjustments are made with sheared and then machined titanium blanks. Initially we had planned to investigate a number of different bend radii but because of the success with a 5t radius bend no other radii were tested. The bending procedure employed by workers in the Sheet Metal Shop follows:

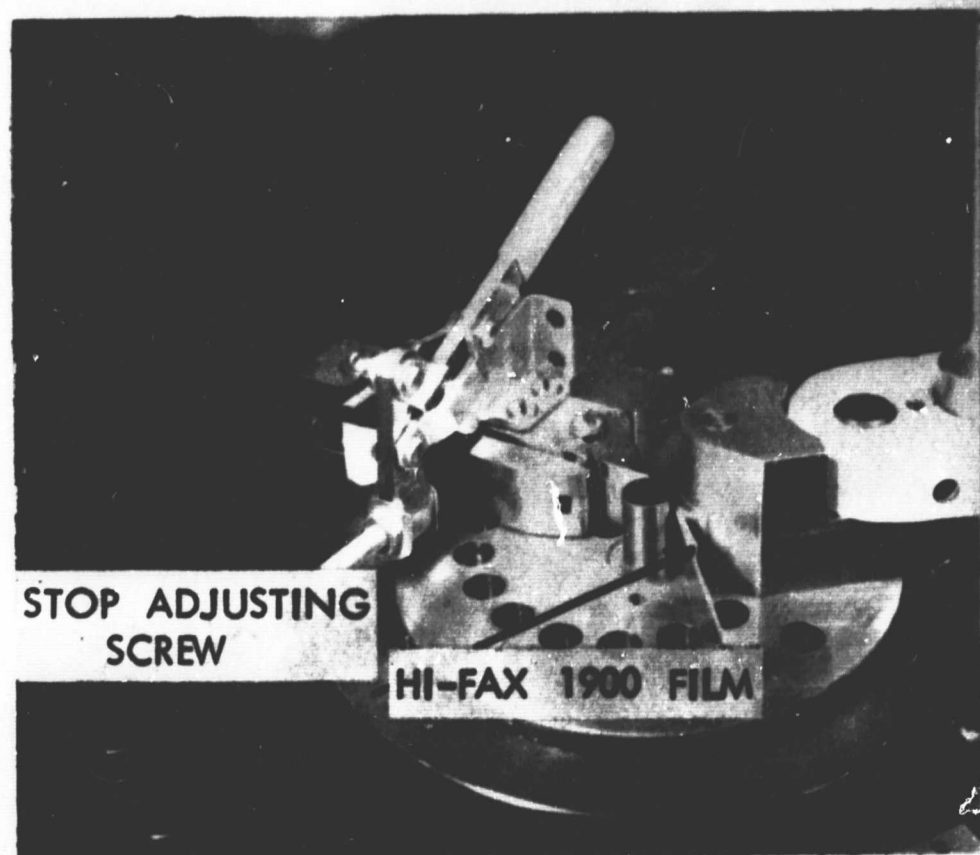
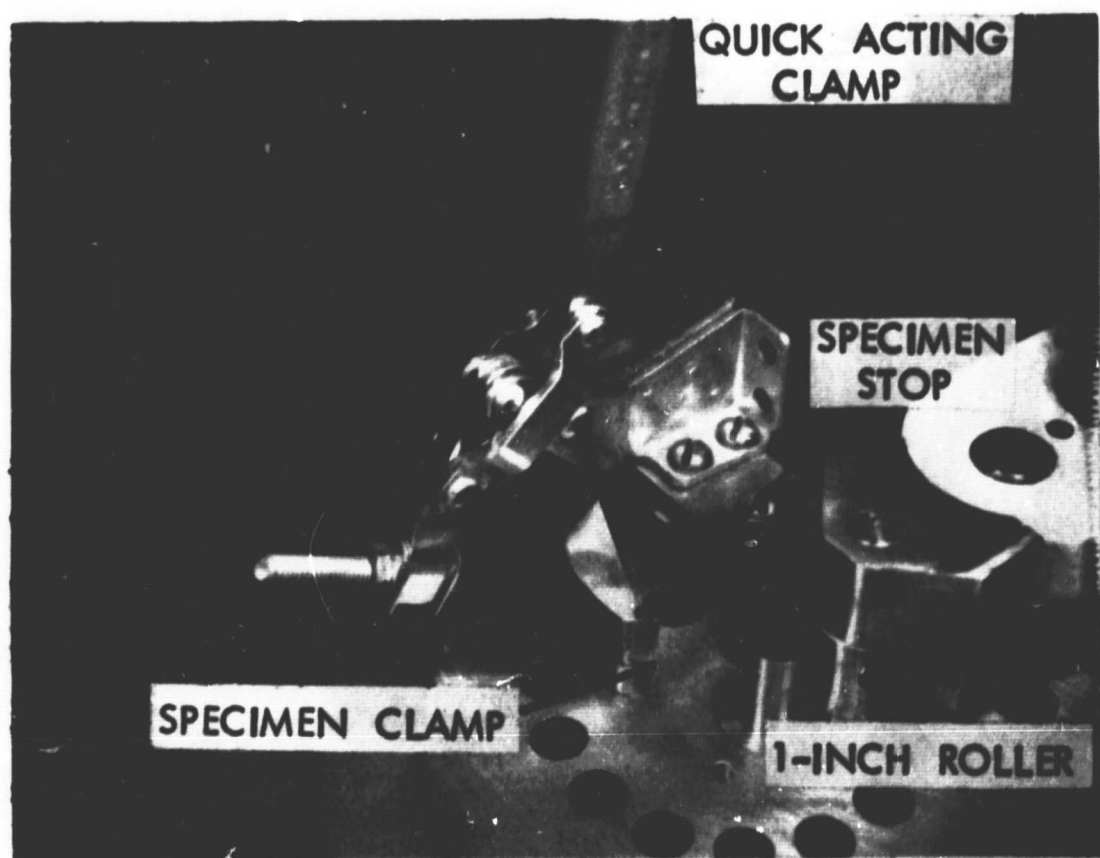
(a) Insert machined blank between the bending mandrel and nosepiece roller until it reaches the specimen stop.

(b) Engage quick acting clamp.

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FIGURE 16

SPECIAL CLAMPING DEVICE INSTALLED ON DI-ACRO BENDER



(b) Mark the center of the line with a small punch;

(c) Stamp U-bend identification marks inside the bend between the loading hole and leg end. Two sets are required.

There are times when the corrosion rate has to be determined on prebend blanks and on U-bends. The corrosion area is the wetted surface of a standard U-prebend. A correction has to be applied for the surface covered by the washers at the loading bolt.

Some typical values obtained from measurement of standard U-prebends are given in Table 8.

### (3) Prebend Cleaning

Clean U-prebends are required for a reproducible surface. The procedure employed for these tests is a modification of the standard procedure employed for corrosion tests at Hercules Incorporated. Basic points are:

(a) Pour reagent grade aluminum oxide in an evaporating dish;

(b) Dip a water wet nylon bristled brush (similar to Beacon Brush and Supply Company, Lab No. 84) in the dish and scrub all large surfaces until they all produce a water flash;

(c) Continue scrubbing under flowing tap water in the absence of additional  $Al_2O_3$  until most of the abrasive has been removed. Finish scrubbing with a clean brush under flowing distilled water until all visible particles of aluminum oxide are removed;

(d) Rinse with distilled water then acetone;

(e) Install specimens on a glass rack, then immerse in boiling, clean acetone for 5 minutes. Remove and dry with hot air gun;

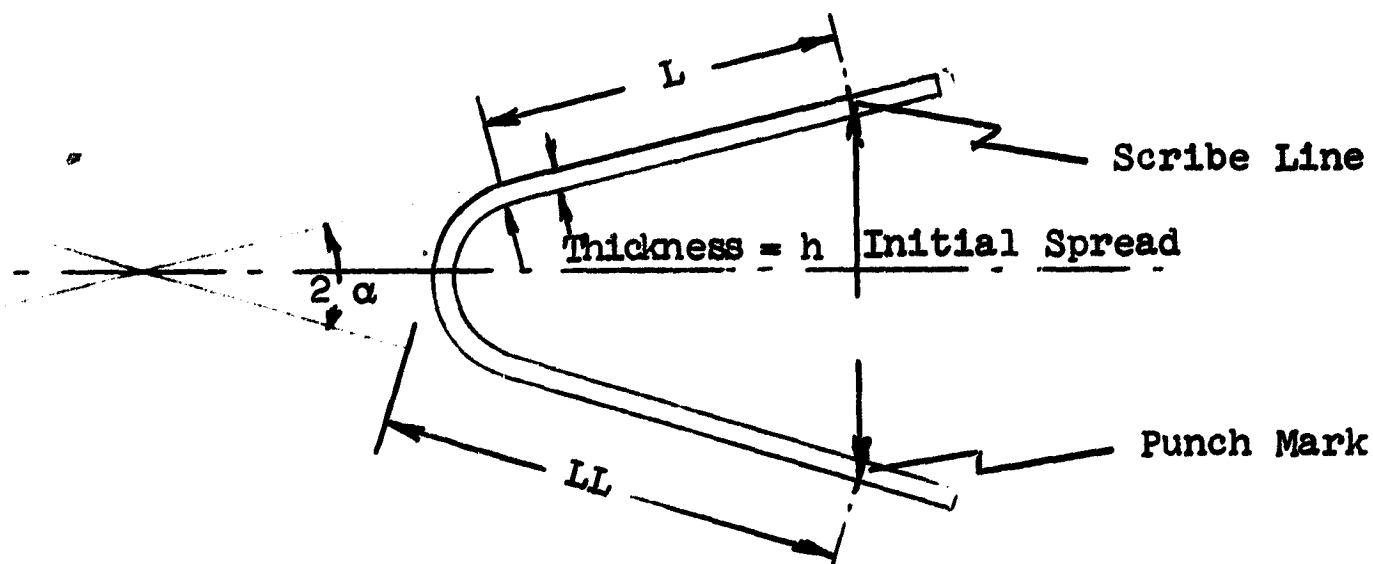
(c) Insert a strip of Hi-fax 1900 tape between blank and nosepiece roller.

(d) Pull the bending arm through an angle of about  $200^\circ$ . While holding the bent leg against the clamping device return the bending arm to its original position.

(e) Release quick acting clamp, remove U-prebend from bender and place in protective envelope.

(2) Measurements Prior to Stressing

The application of the proper amount of stress to a U-bend requires initial measurement of the tangent length, leg length, initial spread, thickness, and the angle included between the U-bend legs (calculation of the U-bend radius is made from the first three dimensions). These measurements are made with an inside/outside dial caliper, 0.005 cm. scale divisions, and machinist's protractor ( $1^\circ$  divisions) at the locations shown below.



Measurements follow the preliminary steps given below.

(a) Scribe a line across the thickness of each leg, at the hole center line. Use a scribing template;

Table 8

Typical Measured and Calculated Values for  
U-Prebends and U-Bends at a Bend Radius of 5t

Measurement	Bend Perpendicular To Rolling Direction (1)			Bend Parallel To Rolling Direction (2)		
	Arithmetic(3) Mean	Standard Deviation	Sample Variance	Arithmetic(3) Mean	Standard Deviation	Sample Variance
Leg Length, cm.	5.02	0.01	0.0001	5.03	0.009	0.00008
Tangent Length, cm.	3.93	0.005	0.000026	3.93	0.008	0.00007
Initial Spread Angle, °	28	0.95	0.9	29.2	0.63	0.4
Initial Spread, cm.	3.89	0.080	0.0064	3.94	0.039	0.0015
Deflection At 90% of Y.S., cm.	1.86	0.038	0.0014	1.89	0.32	0.0010

- 
- (1) Specimens sheared so that the long dimension is in the rolling direction.  
Yield Strength - 136,900 psi., Tensile Strength - 147,700 psi., Elongation - 14.5%.
- (2) Specimens sheared so that the long dimension is perpendicular to the rolling direction  
(transverse). Yield Strength - 139,100 psi., Tensile Strength - 146,400, Elongation - 12.5%
- (3) Based on 10 specimens/set.



(f) Place in clean glassine bags then in a dessicator until the prebends are used;

(g) In the event that corrosion rates are to be determined, weigh U-prebends to the nearest 0.1 mg.

d. U-Bends

(1) Stressing

Premeasured and cleaned prebends are handled with new clean cotton gloves during stressing and installation on the U-bend support rack. Care is taken during loading of the bends that only the bolt head and nuts come in contact with acetone cleaned wrenches and an acetone cleaned vise. Loading is accomplished by advancing a 1/4-inch NC-20 nut on a bolt (nut, bolt and washers are 6 Al, 4 V Ti alloy) until the desired deflection is attained. The deflection is calculated for the previously determined U-prebend dimensions using a formula developed from an article by Blake (8).

The deflection, 
$$Y = \frac{4 S}{E} \frac{r^2}{h} \frac{G}{(1 - \cos \beta + K \cos \alpha)} \quad (1)$$

where E = modulus of elasticity, psi.

G = deflection factor depending on K and  $\beta$ , Eq. (2)

h = thickness of strip cross-section, in.

K = length ratio, L/r

L = length of straight portion of complex-shaped spring, in.

r = mean radius of curvature, in.

Y = deflection, in.

$\alpha$  = angle at which load is applied, radians

$\beta$  = angle subtended by curved portion of spring, radians

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(8) A. Blake, Product Engineering, Oct. 2, 1961, pp. 49-57

$$\text{and } G = \frac{K^3}{3} + K^2 \beta + 2K (1 - \cos \beta) + \frac{\beta}{2} - \frac{\sin 2\beta}{4} \quad (2)$$

Deflections calculated from Eq. (1) have been compared with those determined from the flat spring equations proposed by Palm and Thomas (9) as well as Fleckenstein (10). In all cases the values determined by the Blake formula were higher. The higher values do not establish the validity of the equation, but the Blake values, because they are higher, should provide a more highly stressed U-bend.

The utility of the Blake spring formula for U-bend stressing was further tested by comparing experimentally determined U-bend spring constants ( $\Delta P / \Delta Y$ ) with calculated ones. Experimental constants were -7.5 to +23.7% higher than calculated load:deflection ratios. The experimentally determined load:deflection curves were nearly linear for deflections approaching 0.8 inches. Near this deflection the curve slope decreases suggesting secondary bending or yielding. Near 0.8 inches the legs of the U-bend begin to bow and the radius of the bend no longer contracts. Complete closure of the U-bend, legs just touching, followed by a return to a no-load condition does not produce detectable yielding. Repeats of these experiments with bonded strain gages show zero yielding when the legs have been brought to the just touching position and returned to the unloaded condition.

Our standard prebends, bent at a radius of 5 times the thickness on the modified Di-Acro bender, develop a concavity on the outside of the bend. The concavity is, apparently, a natural response to the

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(9) J. Palm and K. Thomas, Product Engineering, Design Digest Issue, Mid-Sept. 1960, pp. 286-287.

(10) J. E. Fleckenstein, 1960 ASME Annual Meeting, Paper 60-WA-172.

bending process and results in a tensile region developing 1/16-inch wide in from each edge of the specimen on the inside radius of the bend. The tensile stress so produced, is sufficient to induce cracks in prebends after exposure to RR  $N_2O_4$ . The concavity also complicates any stress calculation because of the curvature introduced into the beam in the region of maximum strain (region furthest removed from loading points). On loading, stress reversal must be produced before all portions of the outside of the bend are in tension. Thus there is a variation in stress from edge to edge on any bend specimen under any condition of loading.

## 2. Test Cell Handling

The procedures indicated in this section on test cell handling were used almost routinely during this work. They were developed in part by edict after consideration of different alternatives and in part by evolution. Effects of acetone, for example, as a cleaning solvent were not explored, neither was the need for liquid purges, used with cylinder  $N_2O_4$ , instead of gas purges, as employed with "dried"  $N_2O_4$ . Equilibration times required after  $NO$ ,  $O_2$ ,  $H_2O$ , and  $HNO_3$  additions to RR  $N_2O_4$  or "dried"  $N_2O_4$  or on blending RR and  $G^8$   $N_2O_4$  were not explored sufficiently. In the cases involving blends of RR and  $G^8$ , we noted compositions (%  $NO$ ) different from calculated ones in spite of precautions to eliminate  $H_2O$  from and account for the  $O_2$  in 4 and 9-gallon tanks. Thus, the procedures which follow are more nearly what we did rather than how it should be done. Also, the test cell comments apply to the one

used for 23 runs, Figure 17, and not to the earlier developmental models or the one with stainless steel flanges, Runs 1-2.

(a) Cell Cleaning

(1) Initial

The Corgard pipe and Teflon end plates of the test cell were first rinsed with distilled water then acetone. Each part was washed with an Alconox-water solution, rinsed with distilled water then dried in an 80°C. oven. An end plate was attached to either end, then the assembly filled with Chromerge-conc.  $\text{H}_2\text{SO}_4$  solution and allowed to soak for 15 minutes. The cleaning solution was drained followed by numerous distilled water flushes and a final overnight soak in distilled water. If the water sample had  $<1$  ppm. Cr, the rinses and soak were deemed adequate. A pickle in conc.  $\text{HNO}_3$  followed for 30 minutes. The acid was drained, the cell and parts rinsed with distilled water and oven dried.

(2) Between Runs

Each test cell after a run was emptied, blown free of  $\text{N}_2\text{O}_4$  with  $\text{N}_2$ , one end plate taken off, and the U-bends with their support rack removed for crack examination. Often a white solid residue was present on the glass and Teflon surfaces. This was wiped off with Scott Terri Towels (paper towels). Then all  $\text{N}_2\text{O}_4$  wetted surfaces were rinsed with distilled water followed by an acetone rinse. Acetone was removed by gentle heating of the cell and end plates with a hot air gun. The test cells were then deemed ready for another run.

(b) Cell Pressure Tests

All cells were assembled (Figure 17) with U-bends in place before pressure testing. Nitrogen was purged through the cell for a short time and then the cell was sealed. It was immersed in water, pressured to 50-60 psig.  $N_2$ , bolts tightened, leakage corrected and finally finished off at 150 to 180 psig.  $N_2$ . An acceptable test of the test cell assembly resulted when the nitrogen bubble rate from either end was less than 1 bubble every 5 seconds. Cell pressure was reduced to 50 psig.,  $N_2$  tank fitting disconnected and all piping connections dried. A cell pressure of 50 psig. was maintained until  $N_2O_4$  charging took place.

(c)  $N_2O_4$  Charging

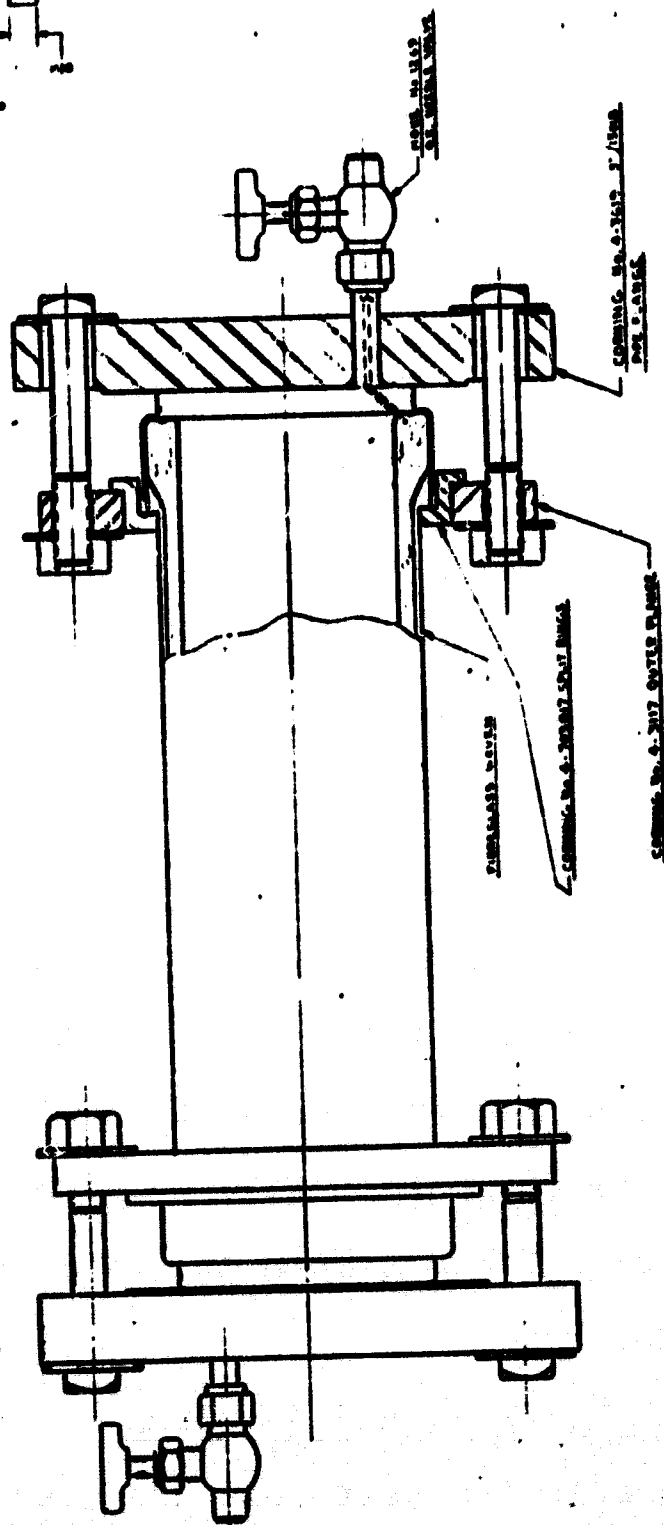
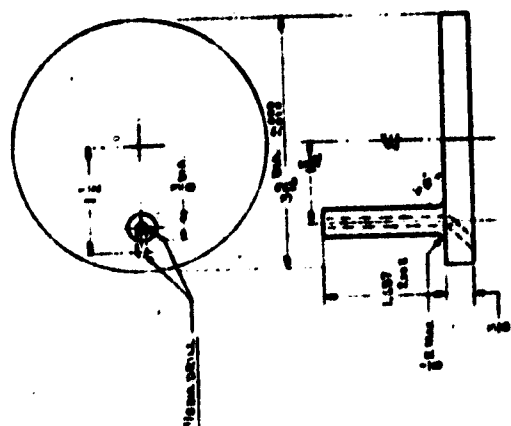
(1) Cylinder  $N_2O_4$

Each waste and filling section of Teflon tubing was first flushed and then filled with nitrogen from the  $N_2O_4$ - $N_2$  manifold. A test cell connected and then the 50 psig.  $N_2$  vented off through the waste receiver.  $N_2O_4$  is introduced into the cell from the 1-ton cylinder until it overflows from the top of the cell into the sight glass of the waste receiver. The  $N_2O_4$  supply is cut off, the cell rocked gently several times and then the cell is emptied by slight  $N_2$  pressure. Again the cell is filled with  $N_2O_4$ , rocked and emptied. After the third filling, 200 ml. of liquid  $N_2O_4$  is vented from the cell to provide ullage during the test at 165°F.

(2) Dried  $N_2O_4$

Test cells were used as intermediate receivers in the drying train. Each cell was first purged with 10 or more volumes of  $N_2$  before the standard pressure test was applied. Thus, oxygen

**FIGURE 17**  
**STRESS CORROSION CRACKING TEST CELL**



**D-72**

[illegible]

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was at a low level prior to the addition of "dried"  $\text{N}_2\text{O}_4$ . The "dried"  $\text{N}_2\text{O}_4$ , obtained by distillation of Red Reactive  $\text{N}_2\text{O}_4$  through Linde 3A Molecular Sieve, was added directly to the test cell from the condenser take-off line, filling from the bottom to the top. Vaporization of  $\text{N}_2\text{O}_4$  occurred until the cell cooled, thus a vapor purge was effected at the beginning. Under distillation-drying conditions, filling usually took one hour because of the drying rate of the system was  $\approx 1,500$  cc. of dry  $\text{N}_2\text{O}_4$  per hour. Liquid  $\text{N}_2\text{O}_4$  overflow from the top part of the cell was usually continued until 100 to 200 cc. had passed into the "dry" waste receiver. At this stage, the cell was bypassed and removed from the drying train.

When more than one cell of "dried"  $\text{N}_2\text{O}_4$  was required, the distillation was interrupted after the first cell was filled. The by-pass around the cell was opened, the cell isolated and valved off then removed from the drying train. A second pressure tested cell was installed at the condenser, vented through the waste receiver, then through 1 liter of active Molecular Sieve and finally to the atmosphere. Filling of the second cell was begun when a fresh charge of RR  $\text{N}_2\text{O}_4$  was placed in the vaporization flask and vaporization heat applied. Only 40% or 1.5 liters of the flask charge was distilled in each filling so the capacity of the Linde 3A Molecular Sieve column for  $\text{HNO}_3$  and other protonated species was not exceeded.

#### d. Cell Ullaging and Sampling

Gases in the test cell are displaced by liquid  $\text{N}_2\text{O}_4$  in the cell charging step whether the source of  $\text{N}_2\text{O}_4$  is the drying train, blend tanks or storage cylinder. Because the cell is completely

full of liquid at this stage, 200 cc. of  $\text{N}_2\text{O}_4$  had to be drained out of the cell to provide thermal expansion room for the oxidant at test temperature. This ullage volume was discarded if the cell was charged from either RR or G8 storage cylinders. Cell charges from other sources had to be sampled first and then, if additions were made directly to the cell, sampled again until a total of 200 cc. was withdrawn. Sample bulbs were of the type described previously (Figure 18A) and usually had 100 cc. capacity. Connections to the bulb and cell were made with a 3/8-inch Beckman Teflon fitting, 3/8-inch Type 304 stainless steel tubing and a Swagelok male tubing connector (Figure 18B). The samples were pushed into the bulb past the Fisher-Porter needle valve in the vapor leg by pressure within the cell. Flow was out the liquid leg so a liquid seal, up to the outlet valve, could easily be maintained on the downstream or waste side of the sample bulb. The valve closing sequence was; first the cell valve, then the liquid valve and finally the vapor valve at the cell-bulb connector. Expansion space in the bulb was created by forcing liquid out through the liquid leg by gentle handwarming. The valves were secured and then the bulb disconnected from the test cell. Any residual  $\text{N}_2\text{O}_4$  in the lines external to the sample space was displaced with nitrogen.

e. Test Cell Emptying

When a test run was made with  $\text{N}_2\text{O}_4$  modified in some way - degassed, "dried", blended G8 and RR, NO added,  $\text{H}_2\text{O}$  treated or  $\text{HNO}_3$  doped - a sample was always taken at the conclusion of the run.



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FIGURE 18A  
 $\text{N}_2\text{O}_4$  SAMPLE BULB

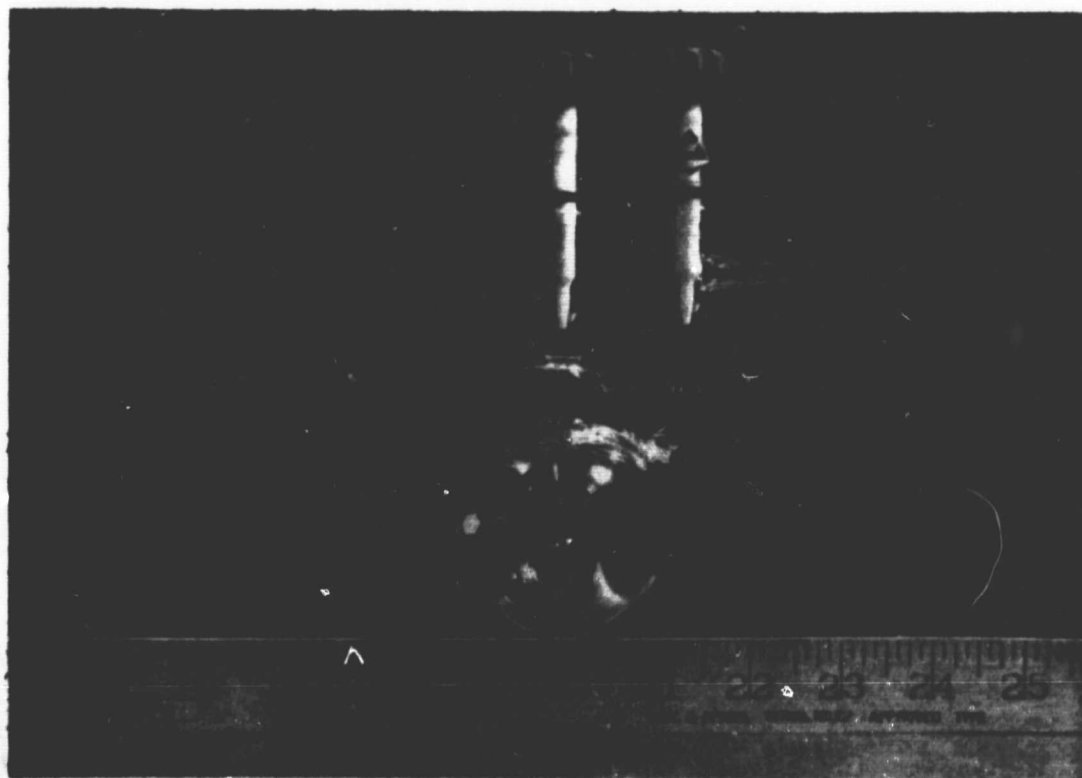
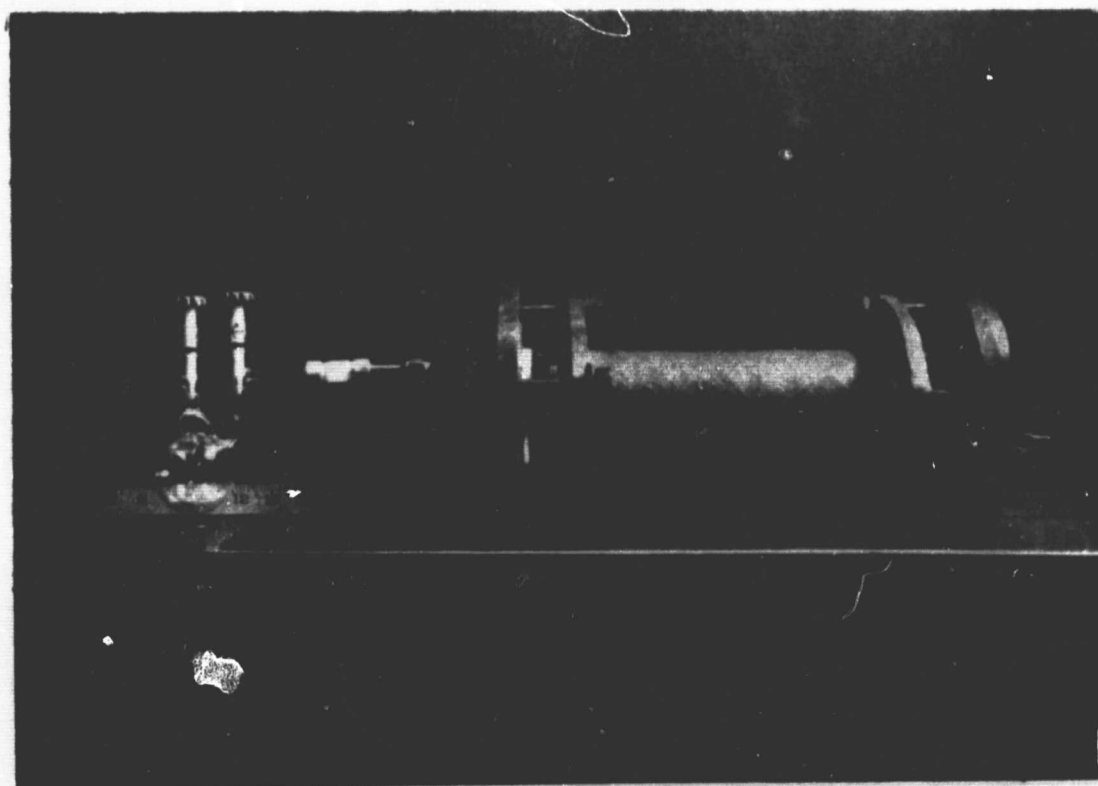


FIGURE 18B  
 $\text{N}_2\text{O}_4$  SAMPLE BULB CONNECTED  
TO SCC TEST CELL



First the cell was removed from the oven and allowed to cool down to 100-120°F. Then a dry, nitrogen purged sample bulb was connected to the liquid or bottom valve of the test cell. Valves were opened permitting all of the liquid  $N_2O_4$  to pass into and most of it through the sample bulb into a waste receiver. The standard bulb disconnect procedure was used followed by a blowdown of the cell. Nitrogen was then purged through until the brown color of  $N_2O_4$  was undetected. The cell was sealed under  $N_2$  until it was opened for examination of specimens.

### 3. Specimen Examination

In those many instances where U-bends cracked in two the specimens were only given a cursory examination. Those U-bends which were intact but with cracks visible to the unaided eye were examined at 40X with a stereomicroscope. Information on the number of cracks at the bend plus the location of other cracks was sought. Almost always, at this stage of the examination, the U-bends were unloaded. They were flexed under the microscope to open up minute cracks. When no cracks were visible, with the unaided eye, on loaded U-bends, the microscopic examination progressed from the stereoscopic examination to examination at 400X. This was how the cracks on 20 specimens from Run 10 and 11, low (1.1 ppm.) and high (20.1 ppm.) oxygen RR  $N_2O_4$  at room temperature, were detected and counted. At least two and often three observers examined every one of the exposed U-bends for cracks. In all cases the specimens were examined as is without benefit of the grinding-polishing-etching customary for metallurgical examinations because the 240 grit surfaces and milled edges were adequate for the purpose.

#### 4. Preparation of Various Types of $N_2O_4$

##### a. RR and $G^8$ $N_2O_4$

The quality of RR and  $G^8$  NO has been described in the first and second Quarterly Reports of this contract. They were produced at the Hercules Incorporated plant at Hercules, California, and were in accordance with both Mil-P-26539B (RR  $N_2O_4$ ) and MSC-PPD-2A ( $G^8$   $N_2O_4$ ) specifications. No nitric oxide (NO) was detected in the RR and upwards of 0.81% NO was found by the MSC-PPD-2A Colorimetric procedure in  $G^8$   $N_2O_4$ . These materials, in 1-ton cylinders, served as the basic stock for all of the formulations which followed.

##### b. $G^4$ (0.40% NO) and RNR (0.05% NO) $N_2O_4$

Both  $G^4$  and RNR  $N_2O_4$  were made by blending RR and  $G^8$   $N_2O_4$  in a 9-gallon or 4-gallon stainless steel oxygen bottle. The first blend of  $G^8$  with RR to produce  $G^4$  was made in a dry vessel filled with air. Instead of a 0.40% NO preparation only 0.355% NO was found. Introduction of additional  $G^8$   $N_2O_4$  brought the composition to the desired range. In the next experiment the blend tank was purged with  $N_2$ , pressured to 20 psig. with  $N_2$ , bled to atmospheric pressure, rinsed with RR  $N_2O_4$ , drained, tared, then the requisite amount of RR and  $G^8$  material introduced. Analysis of the contents revealed 0.050% NO. This  $N_2O_4$  appeared visually red. When tested in Run 8, it did not crack any of the titanium U-bends so it was classed as Red Non-Reactive (RNR)  $N_2O_4$ .

c. 0.01% NO

A series of attempts were made to produce an  $N_2O_4$  which contained 0.01% or 100 ppm. NO with the same  $HNO_3$  and water levels of the basic RR and G8 types. In the first attempt the blend tank was evacuated three times to 1 mm. Hg, repressured with low  $O_2$  nitrogen and finally the required amounts of RR and G8 added. After overnight aging at 80°F. the material was sampled and used for Run 14. Nitric oxide was not detected but the oxygen level of the sample was in the 0.1 to 0.4 ppm. range. An additional quantity of G8 was added to the tank and after aging the solution was again analyzed; no nitric oxide was detected. Once more the calculated quantity of G8 required to convert the blend to 100 ppm. NO was added. This time the material had 36 ppm. NO (it was employed in Run 16). The inability to attain the desired NO level was probably due to the shifting equilibria of the protonated species as additional  $N_2O_3$  was added.

d. Deoxygenation of  $N_2O_4$  by Boiling

Two SCC Runs, 10 and 12, were made in  $N_2O_4$  which was deoxygenated by boiling off a portion of the  $N_2O_4$  in the test cell. In the first instance a test cell with the standard 200 cc. ullage was bled intermittently of  $NO_2$  vapors and oxygen. After about 24 hours the  $O_2$  was reduced to 1.1 ppm. The whole process was monitored by gas chromatography of gas and liquid samples. The next attempt at

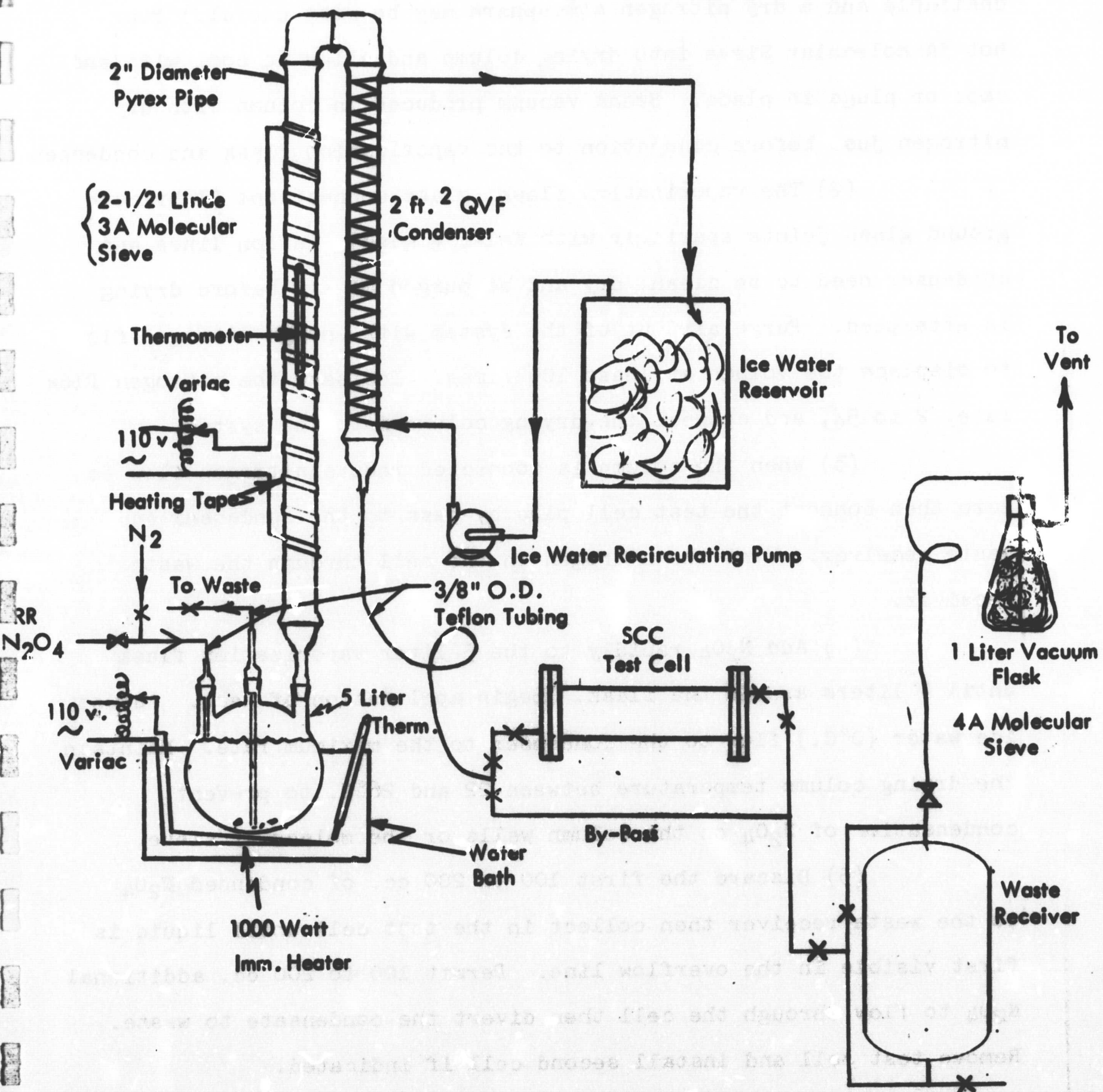
oxygen removal, Run 12, was made with continual vaporization of  $\text{N}_2\text{O}_4$ . Venting from the test cell was at a rate of 8,800 cc./hr. The  $\text{O}_2$  level was at 2 ppm. instead of the expected  $<1$  ppm. Final reduction to 0.08 ppm. was attained by intermittent boil-off with the progress of deoxygenation followed by gas chromatography. The most obvious reason why continuous venting did not reduce the oxygen level sufficiently was the lack of equilibration between liquid and vapor phases. A second reason is, the solubility of  $\text{O}_2$  in  $\text{N}_2\text{O}_4$  increases with temperature (7). In the continuous venting approach, vaporization heat was applied from a hot air gun and it is presumed that the resultant  $\text{N}_2\text{O}_4$  temperature,  $>25$ , was higher than that produced under nominal laboratory conditions, 22 to  $25^\circ\text{C}$ .

e. Dehydrated  $\text{N}_2\text{O}_4$

The "dehydration" or reduction of the proton level in RR  $\text{N}_2\text{O}_4$  was explored and developed because of its importance to the  $\text{NO}-\text{H}_2\text{O}$  study portion of this work. Earlier (Third Quarterly, Page 13) the unsuccessful, drying of  $\text{N}_2$  stream saturated with  $\text{N}_2\text{O}_4$  over  $\text{P}_2\text{O}_5$  coated beads, was described. Also, the successful small-scale preparation of dry  $\text{N}_2\text{O}_4$  by contacting  $\text{NO}_2$  vapors with Linde 3A Molecular Sieve was indicated. As previously discussed, a larger laboratory unit for preparation of  $\text{N}_2\text{O}_4$ , low in the protonated species  $\text{HNO}_5$ , was successfully operated. A product with less than 500 ppm.  $\text{HNO}_3$  (usually  $<300$ ) was prepared from a RR  $\text{HNO}_3$  containing 5,000-6,000 ppm.  $\text{HNO}_3$ . A flowsheet of the "drying" setup is shown in Figure 19 and some of the salient operating points are given below.

FIGURE 19

$\text{N}_2\text{O}_4$  DEHYDRATION TRAIN



(1) Activate Linde 3A Molecular Sieve by holding in an air oven for at least 4 hours at 220°C. (A higher temperature may be desirable and a dry nitrogen atmosphere may be most useful.) Pour hot 3A Molecular Sieve into drying column and allow to cool with end caps or plugs in place. Break vacuum produced in column with dry nitrogen just before connection to the vaporization flask and condenser

(2) The vaporization flask, glass connections (lubricate ground glass joints sparingly with Kel-F grease), Teflon lines and condenser need to be clean, dry and be purged of air before drying is attempted. Purge air out of the system with enough nitrogen flow to displace the volume at least 100 times. Increase the nitrogen flow rate, 2 to 5X, and connect the drying column into the system.

(3) When the column is connected reduce nitrogen flow to zero then connect the test cell plus by-pass to the condenser and waste receiver. Vent the nitrogen in the cell through the waste receiver.

(4) Add  $\text{N}_2\text{O}_4$  rapidly to the 5-liter vaporization flask until 4 liters are in the flask. Begin application of heat. Adjust ice water (0°C.) flow to the condenser to the maximum rate. Maintain the drying column temperature between 22 and 26°C. to prevent condensation of  $\text{N}_2\text{O}_4$  on the column walls or the molecular sieve.

(5) Discard the first 100 to 200 cc. of condensed  $\text{N}_2\text{O}_4$  to the waste receiver then collect in the test cell until liquid is first visible in the overflow line. Permit 100 to 200 cc. additional  $\text{N}_2\text{O}_4$  to flow through the cell then divert the condensate to waste. Remove test cell and install second cell if indicated.



f. H<sub>2</sub>O, HNO<sub>3</sub>, NO and O<sub>2</sub> Additions to N<sub>2</sub>O<sub>4</sub>

Modifications of N<sub>2</sub>O<sub>4</sub> were also attempted by additions to the test cell either by a flow-through procedure or by direct addition to the cell. In the flow-through method (Runs 17 and 18) a known quantity of 99+% HNO<sub>3</sub> or water was introduced into a sample bulb which was connected between the drying train and the test cell. All N<sub>2</sub>O<sub>4</sub> from the drying train passed through the bulb sweeping the additive into the test cell. Unfortunately, mixing was poor in the bulb and backflow through the long lines occurred. This backflow (employed only for Runs 17 and 18) took place when pressure built up in the test cell forcing N<sub>2</sub>O<sub>4</sub> back through the bulb and lines up into the condenser. A cooled test cell or shorter lines could have eliminated this problem, but, before these corrections were applied, this addition approach was abandoned.

The second method employed, Runs 19-25, hypodermic techniques as practiced in gas chromatography. A silicone rubber septum was attached to either the vapor or liquid phase valve and known quantities of gas or liquid were syringed into the test cell. The cell was placed vertical for water addition through the gas phase valve. Gravity and gas pressure generated within the cell was sufficient to move the liquid into the test cell. (No traces of water or HNO<sub>3</sub> were ever found in the space between the valve and septum on disassembly when this liquid addition method was used.) The introduction of gases was made with the cell in its normal horizontal position through the bottom or liquid valve. No liquid N<sub>2</sub>O<sub>4</sub> was ever detected when the septum was disconnected from the test



cell valve. Silicone rubber, septum material, under these conditions has an adequate life with sufficient resilience to seal against hypodermic needles for several hours. In contact with liquid  $N_2O_4$  or 99+%  $HNO_3$  the silicone rubber septum hardens, cracks and generally decomposes. It is adequate for short periods, 5-10 minutes, but contamination of the test fluid and loss of seal would occur with longer periods of contact. Fluoroelastomers (Viton, Fluorel and Kel-F) offer the most hope for resistance to liquid  $N_2O_4$  for septums used this type of addition technique.

#### 5. Safety Precautions

Liquid  $N_2O_4$  is an insidious material in many respects but the most disconcerting behavior in our operations was its tendency to hang up in lines. In numerous disconnects between sample bulbs, other lines and the test cell, the joint would be drained, tapped and adjudged free of  $N_2O_4$ . Invariably some  $N_2O_4$  would cling to a valve stem, hang up in a fitting or other location. Where the equipment was transparent, the  $N_2O_4$  would be discovered when a brown stain formed on the blue neoprene rubber gloves that were always worn when the material was being processed. On occasion, large amounts issued from an opening in excess of the capacity of the glove to absorb the  $N_2O_4$ . In this case and all other cases of spill, the area of potential skin contact was washed immediately with water.

Another problem in re-use and re-connection of fittings, valves, tubing and other components is the tendency for  $HNO_3$  to form from residual  $N_2O_4$  and moisture in the air. All parts need to be handled with rubber gloves, washed with water, rinsed with acetone and dried with a hot air gun before they can be re-used.

Eye and face protection were usually maintained with safety glasses and a full face shield. The face shield was adequate for splashes but often NO<sub>2</sub> vapors collected between the shield and the face. Usually this occurred when one bent over the part to be worked on instead of maintaining some horizontal distance between the part and face. In all cases where a series of manipulations or connections external to the hood were, a fresh air mask was used. It was always turned on ready for use whenever operations like drying were in progress.

## II. DETERMINATION OF COMBINED NO IN N<sub>2</sub>O<sub>4</sub> BY VISIBLE SPECTROPHOTOMETRY

Nitric oxide dissolved in liquid N<sub>2</sub>O<sub>4</sub> reacts with equilibrium amounts of NO<sub>2</sub> to form N<sub>2</sub>O<sub>3</sub>. The presence of N<sub>2</sub>O<sub>3</sub> imparts a green color to N<sub>2</sub>O<sub>4</sub>. The concentration of N<sub>2</sub>O<sub>3</sub> can be determined by a spectrophotometric measurement of the absorbance difference between 700 m $\mu$  (maximum) and 900 m $\mu$ . (baseline) at subambient temperatures. A special refrigerated stainless steel cell is employed. Using a 2 mm. path length cell and a 0 to 2.0 absorbance scale, NO can be determined in the 0.3 to 2.0% range with a precision of about 2-3% of the amount present; with a 10 mm. path length cell, NO in the 400 to 4000 ppm. range can be measured with the same precision. To obtain maximum sensitivity of this method, a 10 mm. path length cell and a 0 to 0.2 absorbance scale expansion is used. Under these conditions 0 to 400 ppm. can be measured with a precision of about  $\pm 15$  ppm. NO at the lower levels.

### Apparatus

(1) Spectrophotometer, Recording, Cary 14 or equivalent - capable of measuring absorbance between 700 and 900 m $\mu$  of 0 to 2.0 and with scale expansion 0 to 0.2 absorbance full scale.

(2) Special cell (see Figure 10). Stainless steel block, ported for circulating refrigerant, inlet and outlet valves of inert material, NIR silica windows, adjustable from 2mm. to 10 mm. path length. Outer "storm windows" are fitted on a collar of poor heat conducting material and the space between the inner and outer windows is purged with dry air to prevent moisture condensation on the cold inner windows.

(3) Circulating cooling bath capable of maintaining cell block at  $-10^{\circ}\text{C}$ . (Forma Model 2095-2, or equivalent).

Teflon tubing and assorted fittings of inert materials (Teflon, Kel-F, stainless steel) for transferring  $\text{N}_2\text{O}_4$  from sample vessel to cell without contamination by exposure to air, moisture or other reactive materials.

#### Procedure

The cell, fittings and tubing are flushed successively with water, ethanol, ethyl ether, and dry nitrogen. The valves are closed, the storm window purge is connected and the cell chilled to  $-5^{\circ}\text{C}$ . to  $-10^{\circ}\text{C}$ . The cell and tubing is then briefly purged with dry nitrogen, the inlet tube is quickly connected to the  $\text{N}_2\text{O}_4$  sample container and the outlet tube to a waste receiver. About 10 ml. of  $\text{N}_2\text{O}_4$  is bled through the cell before the valves are closed to trap the sample in the cell. The cell is placed in the spectrophotometer, the refrigerant and window purge lines connected, and when the cell temperature reaches  $-10^{\circ}\text{C}$ ., the spectrum is obtained from about 1000  $\text{m}\mu$ . to 600  $\text{m}\mu$ . using a slit setting of 0.20 mm. at 700  $\text{m}\mu$ . The absorbance at 900  $\text{m}\mu$ . is subtracted from that at 700  $\text{m}\mu$ . to obtain  $\Delta A_{700-900 \text{ m}\mu}$ . The NO content is then calculated as follows:

$$(1) \quad \text{ppm. by wt. NO} = \frac{(\Delta A_{700-900} - C) \times 10^4}{a \times b}$$

where  $A_{700-900}$  = is the measured absorbance difference

$C$  = the blank correction, e.e., the  $\Delta A_{700-900}$  of a sample of  $\text{N}_2\text{O}_4$  containing no NO.

$a$  = the calculated absorbance of a sample of  $\text{N}_2\text{O}_4$  containing 1.00% NO in a 10.0 mm. cell.

$b$  = the actual cell path in cm.

### Calibration of the Spectrophotometer

The procedure was originally calibrated by the use of specially prepared samples of  $N_2O_4$  containing known concentrations of NO.  $N_2O_4$  was dried by distillation through 3A mole sieve, oxygenated to oxidize all NO to  $N_2O_4$ , degassed to remove all excess oxygen and then NO was added in known amounts using a glass vacuum line. The relationship of NO concentration to absorbance difference between 900 and 700  $m\mu$  was shown to be linear from 25 ppm. through 15,000 ppm. It is therefore necessary to locate only two points to calibrate any instrument. One is obtained by experimentally measuring in a 1.0 cm. cell the  $\Delta A_{700-900 m\mu}$  of a sample of  $N_2O_4$  which has been oxygenated to remove all NO. It is unnecessary to degas the sample as oxygen does not interfere. This value is also used as "C", the blank correction, in equation (1). The other point can be obtained by measuring the  $\Delta A_{700-900 m\mu}$  of a calibrated glass filter whose spectrum resembles that of  $N_2O_3$ , and whose  $\Delta A_{700-900}$  has been related to a specific concentration of NO in  $N_2O_4$  on the same spectrophotometer on which the original calibration samples were run. A limited number of calibrated filters are available from Hercules Incorporated on request. The standard absorbance "a" for equation (1) may then be calculated as follows:

$$a = \frac{F - C}{S}$$

where  $a$  = the  $\Delta A_{700-900}$  of  $N_2O_4$  containing 1.00% NO in a 1.00 cm. cell at  $-10^\circ C$ .

$F$  = the measured  $A_{700-900} m\mu$  of the filter

$C$  = the measured  $A_{700-900} m\mu$  of the NO-free sample of  $N_2O_4$  in a 1.0 cm. cell at  $-10^\circ C$ .

$S$  = the NO concentration equivalent in percent NO of the calibrated filter

$a$  should be approximately 3.0

### III. DETERMINATION OF TOTAL PROTONATED SPECIES IN $N_2O_4$ BY NMR

Protons exchanging rapidly between different chemical and magnetic environments, such as a mixture of  $H_2O$ ,  $HNO_2$ , and  $HNO_3$  in liquid  $N_2O_4$ , give a single absorption peak in nuclear magnetic resonance spectroscopy (NMR). Since the area of the observed peak is proportional to the number of protons in the sample, the peak may be used for the quantitative determination of the "total protonated species" taking part in the equilibrium. Calibration is accomplished by adding a known amount of a proton-containing internal standard to the sample, since the calibration factor (area/wt. protons) is the same for both the sample and internal standard peaks.

In this procedure, the total protonated species content of the sample is expressed as %  $H_2O$ , since the composition of the exchanging mixture cannot be determined from the NMR spectrum. Benzene is used as the internal standard, and the amount of benzene added to the sample is optimum for samples containing 0.05 to 0.5 %  $H_2O$ .

A quantitative study of the method has shown that in the 0.05 to 0.5%  $H_2O$  range, a relative standard deviation of 5-10% is obtained.

#### Apparatus

(1) NMR Spectrometer - Varian A-60A or equivalent. Must be capable of controlled temperature operation ( $\pm 0.5^\circ C.$ ) in the 0 to  $-10^\circ C.$  range.

(2) NMR Sample Tubes - NMR Specialties, Inc., Type E precision NMR sample tubes, capped with Catalog No. 15-104 polyethylene pressure-tight caps.

(3) Sampling System - The apparatus used for filling the NMR sample tubes from the flasks used to transfer  $\text{N}_2\text{O}_4$  samples in the present program is shown in the Figure 20. In order to reduce contamination of the sample by water adsorbed on the walls of the sample tubes and filling system, all glass parts were heated at  $110^\circ\text{C}$ . in an oven for two hours, then cooled in a desiccator before use. High purity laboratory cylinder nitrogen, from Air Products Corp., was used to flush the sampling system during use.

(4) Microliter Syringe, 50  $\mu\text{l}$ . capacity. Calibrate by injecting at least five successive 20- $\mu\text{l}$ . volumes of benzene into a tared weighing bottle fitted with a rubber stopple. Weigh the bottle to the nearest 0.1 mg. after each addition. Calculate the average weight of benzene delivered by the syringe.

#### Sample Preparation

(1) Assemble the sample filling system as shown in Figure 20, and flush 5-10 ml. of  $\text{N}_2\text{O}_4$  through the system to remove adsorbed water, collecting the waste  $\text{N}_2\text{O}_4$  in a suitable waste receiver.

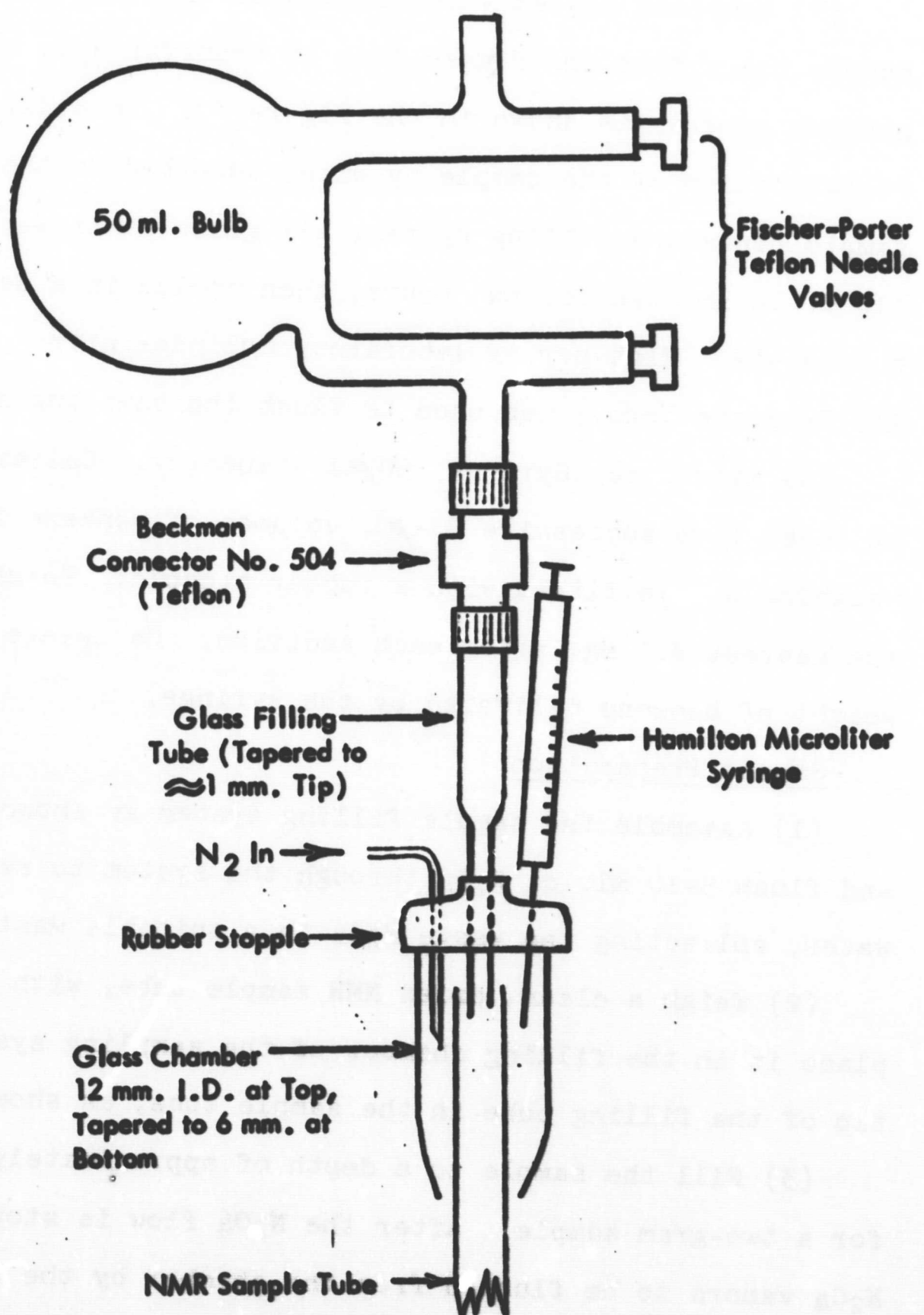
(2) Weigh a clean, dried NMR sample tube, with cap, and place it in the filling chamber of the sampling system with the tip of the filling tube in the sample tube, as shown.

(3) Fill the sample to a depth of approximately four inches, for a two-gram sample. After the  $\text{N}_2\text{O}_4$  flow is stopped, allow the  $\text{N}_2\text{O}_4$  vapors to be flushed from the chamber by the  $\text{N}_2$  flow, remove



FIGURE 20

NMR SAMPLE TUBE FILLING SYSTEM



the sample tube from the filling tube, and place the top of the sample tube near the stopple in a convenient position for addition of the internal standard.

(4) Add 20 ~~μ~~l. of benzene to the sample by means of the calibrated microliter syringe inserted through the stopple. Lower the sample tube out of the filling chamber, cap, mix thoroughly, and weigh the filled sample tube.

#### NMR Spectrum

The spectrum of the sample is obtained using standard instrument conditions for the Varian A-60A spectrometer, except that the sample probe is maintained at approximately -5°C. to prevent boiling of the sample. The peak areas are measured by running the integral spectrum of the sample. Typical instrument settings for the spectral scan are:

Filter Bandwidth = 1.0 Hz

R. F. Field = 0.02 mG

Sweep Time = 250 sec.

Sweep Width = 250 Hz

Spectrum Amplitude = 25

For the integral scan, the R. F. Field was increased to 0.2 mG, the Sweep Time was 100 sec., and the Integral Amplitude was set at 32.

Calculation of Results

The concentration of protonated species in the sample is calculated from the expression:

$$\text{wt. \% H}_2\text{O in N}_2\text{O}_4 = \frac{69.19 \times W_B \times A_{\text{H}_2\text{O}}}{W_S \times A_B}$$

where  $W_B$  = weight of benzene added, grams

$W_S$  = weight of sample taken, grams

$A_{\text{H}_2\text{O}}$  = area of "water" peak

The numerical constant includes the molecular weights of benzene and water, and the number of protons in each molecule.

IV. DETERMINATION OF PROTONATED SPECIES IN  $N_2O_4$  BY  
NEAR-INFRARED SPECTROPHOTOMETRY

The protonated species present in liquid  $N_2O_4$  are  $HNO_3$ ,  $HNO_2$ , and  $H_2O$ . All three of these compounds can participate in the complex equilibrium of the  $N_2O_4$  system. These compounds also exhibit characteristic absorption bands in the 1.3-2.0  $\mu$  region of the infrared spectrum that can be used for qualitative and quantitative analysis. The absorption bands used for analysis in liquid  $N_2O_4$  are:

1.405 $\mu$	$H_2O$	OH stretch overtone
1.45 $\mu$	$HNO_2$	OH stretch overtone
1.47 $\mu$	$HNO_3$	OH stretch overtone
1.90 $\mu$	$H_2O$	OH stretch - HOH deformation combination.

The method has been calibrated for  $HNO_3$  over the range of 200 to 10,000 ppm.; calibrations for  $H_2O$  and  $HNO_2$  have not been performed.

Apparatus and Procedure

The apparatus and procedure are identical to those described in the method for the Spectrophotometric Determination of Combined NO in  $N_2O_4$  except that the spectrum is scanned from 2.0 to 1.3  $\mu$ . Normally, the 10 mm. cell and 0 to 0.2 absorbance scale expansion are used and the slit is set at 0.15 mm. at 1.40  $\mu$ .

The presence of  $H_2O$  and/or  $HNO_2$  may be qualitatively ascertained by the presence of a band at 1.405  $\mu$  and a band or shoulder at 1.45  $\mu$ , respectively.

$HNO_3$  is measured by drawing a baseline tangent to the minima at about 1.425 and 1.525  $\mu$ . The absorbance A is measured at 1.47  $\mu$  between the curve and the baseline.

### Calibration of Spectrophotometer

A sample of  $\text{N}_2\text{O}_4$  was dried by distillation through 3A Molecular Sieve, and oxygenated to remove NO. A Research & Industrial Instruments Co. Model F-07 High Pressure UV Cell, 5.85 cm. pathlength was modified as follows. (See Figure 8). The thick UV silica windows were replaced by thin (1 mm.) IR silica windows; outer, antifog windows similar to those on the special 1 cm. cell were added; an adapter was made to replace a fill plug and permit attachment of a Kel-F-Teflon Hamilton valve; a Swagelok fitting was added to the fill pipe on the cell to permit the use of a septum; the cell block mount was drilled to permit circulation of coolant.

Dry oxygen was purged through the cell for several minutes, the septum sealed, the valve closed, and the cell weighed. The bulb of dry  $\text{N}_2\text{O}_4$  was then connected to the cell valve and the cell was filled while venting through a hypodermic needle inserted in the septum. The cell is designed so that an overhead space can remain after the liquid level is above the top of the windows. The cell was reweighed and the weight of  $\text{N}_2\text{O}_4$  recorded (22.6243 g.). The cell was placed in the cooling block and the whole assembly was placed in the spectrophotometer and cooled to  $0^\circ\text{C}$ . The spectrum from 1.6 to  $1.3\mu$  was then scanned.  $50\mu\text{l.}$  of 99%  $\text{HNO}_3$  was injected through the septum with a syringe, the cell shaken thoroughly, and the spectrum rescanned. This was repeated with five  $10\mu\text{l.}$  additions and three more  $50\mu\text{l.}$  additions of  $\text{HNO}_3$  scanning after each addition. The weight of  $\text{HNO}_3$  added was calculated from its density at room temperature (1.503). The absorbance at  $1.47\mu$  in the 5.85 cm. cell was recorded

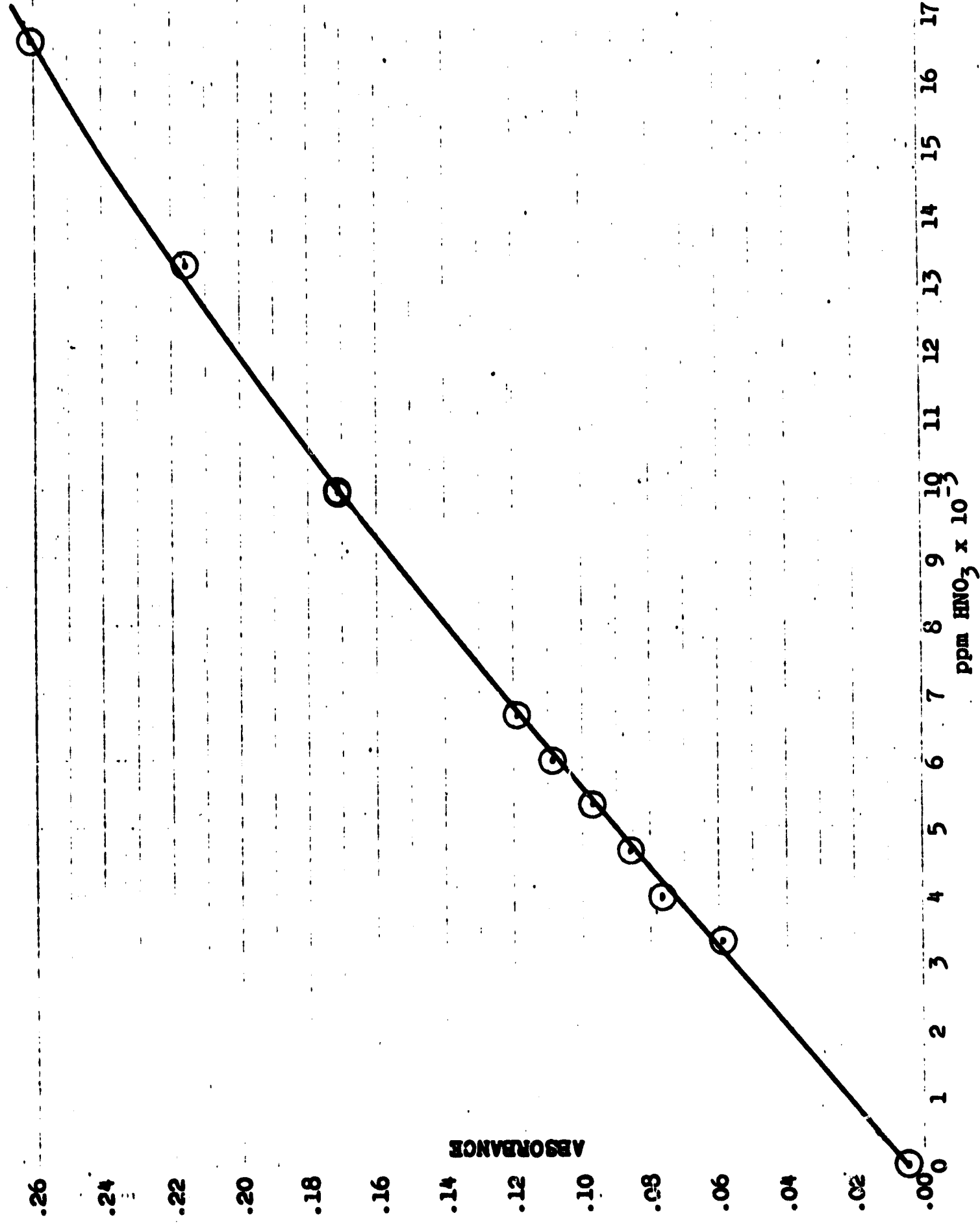
and also calculated for a 1.00 cm. cell. The concentration of  $\text{HNO}_3$  in ppm. was then plotted against the absorbance in a 1.00 cm. cell. See Table 9 and Figure 21. Over the normal working range of 0 to 10,000 ppm.  $\text{HNO}_3$  the calibration curve is sufficiently linear that the absorbance/concentration ratio could be used in place of the curve. This ratio was 0.164 absorbance/1.00%  $\text{HNO}_3$ .

TABLE 9  
CONCENTRATION OF HNO<sub>3</sub> IN N<sub>2</sub>O<sub>4</sub> VS. ABSORBANCE AT 1.47 $\mu$

Total HNO <sub>3</sub> Added		Absorbance at 1.47 $\mu$		HNO <sub>3</sub> conc. in ppm.
<u><math>\mu</math>l</u>	<u>mg. (<math>\mu</math>l. x 1.503)</u>	<u>5.85 cm. cell</u>	<u>Cal'd for 1.00 cm. cell</u>	
0	0	0.033	0.0056	0
50	75.2	0.350	0.0598	3320
60	90.2	0.450	0.0769	3990
70	105	0.505	0.0863	4650
80	120	0.570	0.0974	5310
90	135	0.635	0.1085	5980
100	150	0.700	0.1196	6640
150	225	1.005	0.1718	9970
200	301	1.270	0.2171	13290
250	376	1.540	0.2632	16610

Figure 21

Calibration Curve -  $\text{HNO}_3$  in  $\text{N}_2\text{O}_4$





## V. DETERMINATION OF DISSOLVED OXYGEN IN $N_2O_4$ BY GAS CHROMATOGRAPHY

The following procedure is designed for the determination of oxygen (or other gases) in liquid dinitrogen tetroxide ( $N_2O_4$ ), and in the gas phase above liquid  $N_2O_4$ . Basic to the method is the isolation of the  $N_2O_4$  sample from the atmosphere by means of an inert-low oxygen atmosphere.

Under the conditions used, the limit of oxygen detection by direct analysis of the liquid phase is about 1 ppm. By analysis of the gas phase and computation, through Henry's Law, of the concentration of oxygen in the liquid phase, the range of oxygen detection can be extended to about 10 ppb. in the liquid.

### Apparatus

A schematic diagram of the apparatus in current use is shown in Figure 22. A detailed diagram of the glove bag arrangement used to isolate the sample from atmospheric oxygen is shown in Figure 23.

(1) Gas Chromatograph - Isothermal, hot wire thermal conductivity detector.

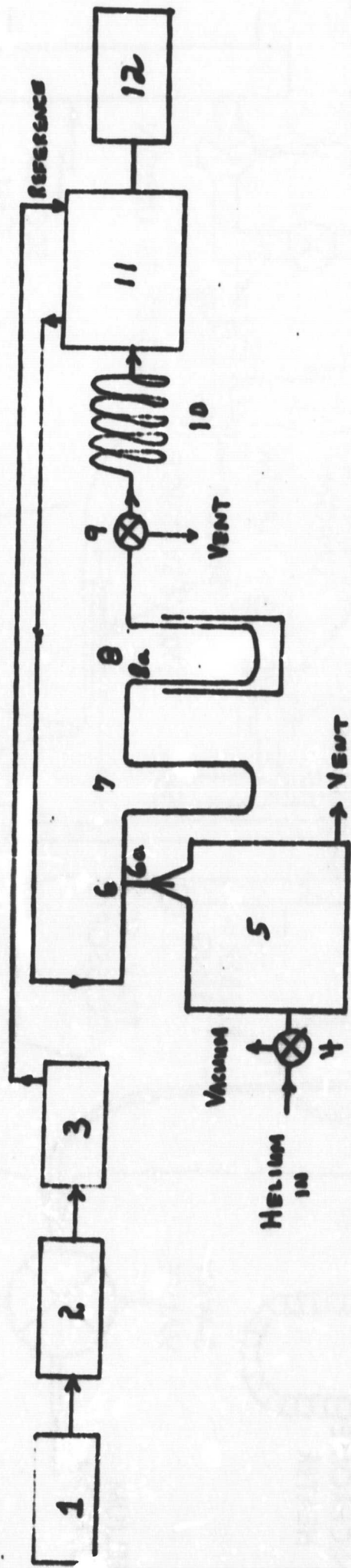
(2) Column - 12 ft. x 1/4 inch O.D. stainless steel packed with Reagent 2 (~53 grams).

(3) Cold Trap - 1 ft. x 1/4 inch O.D. stainless steel shaped in the form of a "U".

(4) Heaters - Two, 18 gauge Nichrome wire (about 12 feet) insulated with spaghetti and wrapped about cold trap and pre-column. Connect each to a variable voltage supply.

Figure 22

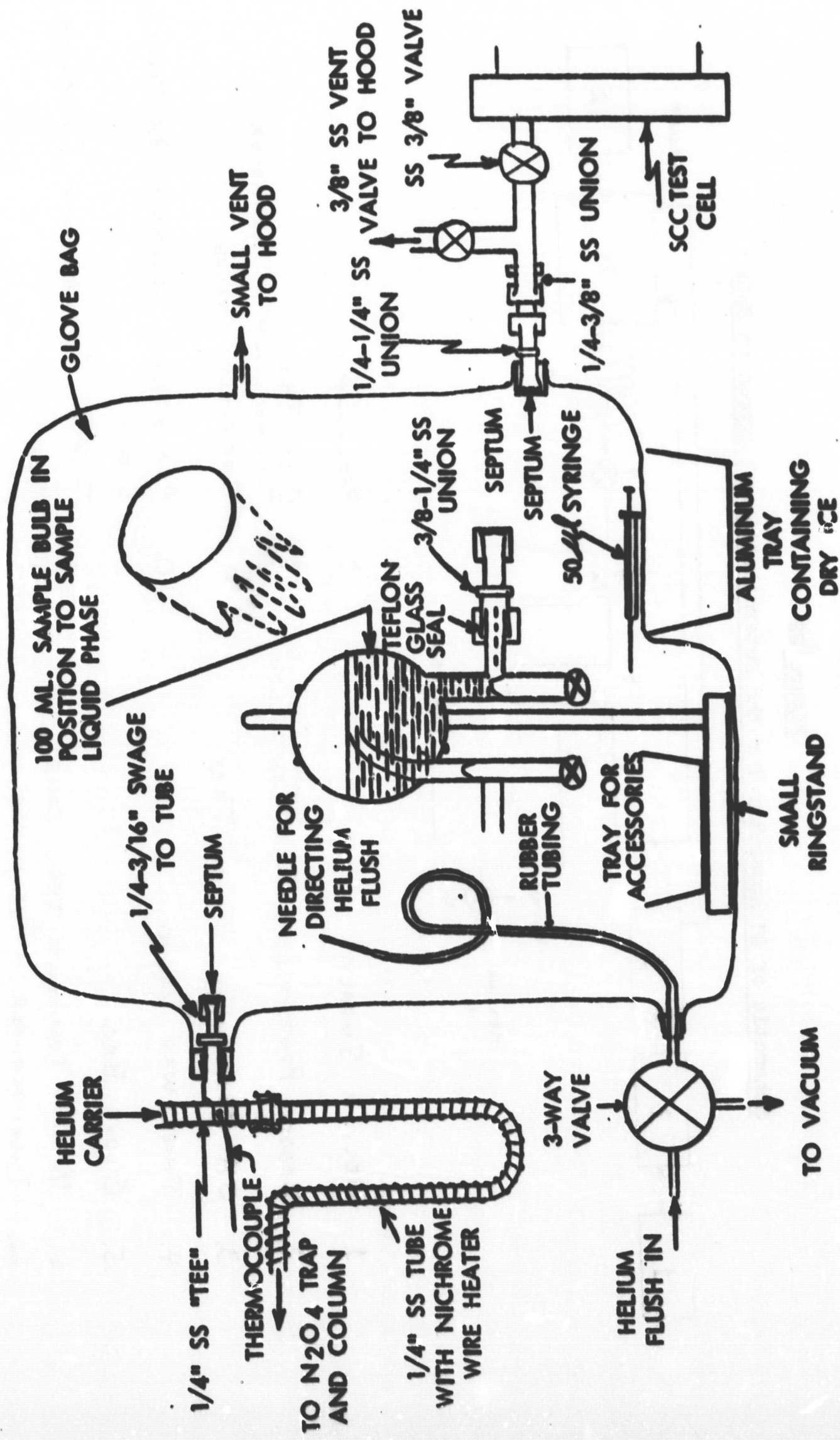
Schematic of GC Apparatus for the Determination of Oxygen in  $H_2O_4$



- |    |                                     |    |   |
|----|-------------------------------------|----|---|
| 1  | HELIUM SUPPLY                       | 7  | PRESSURE COLUMN                         |
| 2  | BROOKS PROPORTIONAL FLOW CONTROLLER | 8  | COLD TRAP THERMOCOUPLE + PYROMETER      |
| 3  | 5A MOLECULAR SIEVE TRAP             | 9  | THREE-WAY VALVE                         |
| 4  | THREE-WAY VALVE                     | 10 | ANALYTICAL COLUMN - 13X MOLECULAR SIEVE |
| 5  | GLOVE BAG                           | 11 | THERMAL CONDUCTIVITY DETECTOR           |
| 6  | 1/4 INCH SWAGELOK TEE INLET         | 12 | RECORDER                                |
| 6a | THERMOCOUPLE + PYROMETER            |    |   |

FIGURE 23

GAS CHROMATOGRAPHIC SAMPLING SYSTEM



(5) Inlet - 1/4 in. O.D. stainless steel "Tee". Fit the center tap with a 3/16 in. to 1/4 in. Swagelok-to-tubing reducer.

(6) Glove Bag - Model X-17-17 obtainable from Instruments for Research and Industry, 108 Franklin Ave., Cheltenham, Pa. 19012.

(7) Hypodermic Syringes - 10, 50, 100 microliter capacities, with fixed chromatographic needle.

(8) Syringes, Gas - 1 and 2 ml. capacities - Pressure Lok available from Precision Sampling Corporation, P.O. Box 15119, Baton Rouge, Louisiana, 70815, Cat. Nos., 206001, 206002.

(9) Fittings - All fittings used in construction of the pre-column accessories and sampling ports should be prepared from stainless steel and/or Teflon parts.

(10) Sample Bulbs - The N<sub>2</sub>O<sub>4</sub> sampling bulb (50 or 100 ml. capacity) is shown in Figure 18A. The valves are of Teflon from Fisher Porter. The sidearms must be constructed to accept a 3/8 inch O.D. Swagelok union. 10 mm. O.D. thick wall glass has been found satisfactory.

(11) Pre-Column - 1 ft. x 1/4 in. O.D. stainless steel tube. See Figure 22 for configuration. This may be packed with a chromatographic column packing or left empty. Wrap with a Nichrome wire heater.

(12) Ring Stand - Cut down so as to fit inside of the glove bag (base ~12 x 18 cm., post ~16 cm.).

(13) Clamp - Multipurpose clamp - Cut attachment arm to ~1 inch, and attach to ring stand.

(14) Aluminum Trays - Two 10 x 20 x 4 cm. Place one inside of glove bag to hold accessories. Use the other to hold dry ice to cool a syringe for liquid sampling.

(15) Valves - Two three-way aluminum with a Teflon core. Attach one to the helium source used to flush the bag. Attach also a source of vacuum. Use the other valve as a vent for the cold trap. See Figure 23.

(16) Septums - (1) Silicone 9.5 mm. diameter to fit 1/4" Swagelok nut. (2) With a No. 4 cork borer cut a septum to fit the 3/16" nut on the inlet to the chromatograph. Cut from a 9.5 mm. septum. Place a supply of each type of septum in the glove bag.

(17) Hypodermic Needles - 2 inch and 6 inch x 15 gauge. Attach one, as needed, to inert gas supply with an 18-inch piece of rubber tubing inside glove bag.

(18) Dewar Flask - 1 pint capacity.

(19) Drying Tube - 12 ft. x 3/8 inch O.D. copper coil.

(20) Thermocouples - Two iron constantan. Locate one on the inlet and one on the cold trap by wrapping with glass tape. Attach each to a Fisher 0° to 500°C. pyrometer, Model 32-J.

#### Reagents

(1) Linde 5A Molecular Sieve. Pack the drying tube with this reagent and activate at 300°C. for 24 hours under helium flow.

(2) Linde 13X Molecular Sieve. Pack the chromatographic column with ~53 grams of this material and activate at 300°C. for at least 4 hours under helium flow.

(3) Trichlorethylene, practical for dry ice trap.

Gas Chromatographic Conditions

Temperatures: - Column, Injection Port, and Detector all at ambient (24-27°C.)

Filament Current: 250 milliamperes

Carrier Gas - Helium at 40 milliliters/minute

Cylinder Pressure - 40 psi.

Recorder - Brown, 1 mv., 1 sec. full scale

Chart Speed - 40 inches/hour

Cold Trap - Dry ice trichloroethylene (-78°C.)

Calibration

To calibrate for oxygen, inject volumes of air varying from 3.0 to 400 microliters into the gas chromatograph. Determine the oxygen peak area in square centimeters by triangulation. Calculate the amount of oxygen injected ( $\mu$ g.  $O_2$ ) in micrograms from the gas laws where

$$g. O_2 = \frac{M \times P \times V}{RT} \quad (1)$$

where M = gram-molecular weight of oxygen = 32

P = pressure

V = volume of air injected

R = gas constant = 0.0821 l-atm./°K-mole

T = absolute temperature

Since air is ~20 percent oxygen

$$\mu g. O_2 = \frac{32 \times 1 \text{ atm.} \times \mu l. (\text{air}) \times 0.2099}{0.0821 \times T^\circ K}$$

$$\mu g. O_2 = \mu l (\text{air}) \times 81.81/T^\circ K. \quad (2)$$



Calculate the response factor,  $F$ , by dividing the micrograms of oxygen injected by the area of the oxygen peak. Run each level of oxygen at least three times and calculate the average response factor at each level. The relative standard deviation for  $F$  should be 2% or less over the 0.8 to 108 microgram range.

#### Procedure

With the gas chromatograph set at the above conditions, load, into the glove bag, the syringes, septa, and other apparatus needed for the determination. Mount the  $N_2O_4$  sample bulb in an upright position on the ring stand. Leave the clamp which holds the shortened multipurpose clamp loose so that the bulb may be rotated freely. Orient the sample sidearm (the arm containing the 3/8 in. to 1/4 in. Swagelok fitting with 3/8 in. Teflon ferrules for the glass seal) so that it points away from the gas chromatograph for sampling the gas phase or toward the chromatograph if the liquid phase is to be sampled. Fit a 1/4 in. stainless steel nut with a 9.5 mm. septum and place in the aluminum tray inside the glove bag. Do not attach to the sample bulb.

Seal the opening to the main body of the gas bag by rolling up the plastic and holding together with the clamps provided with the bag. (Fisher ball joint clamps also work well). Leave a small opening so that gas can be vented at a fairly rapid rate. Begin flushing the bag with helium. Introduce helium at a fast enough rate so that the bag is partially inflated and so that reasonable flushing action is taking place. Direct the helium,

by means of the hypodermic needle-tubing arrangement so that the sidearm or other sampling tube which is to be sealed off is thoroughly flushed with helium. Continue the flushing operation for 30 to 60 minutes, or until the oxygen level has been reduced to less than 0.01%. (See below) Actually levels of less than 0.005% have been attained.

Determine the oxygen level in the glove bag by injection of a 2.0 ml. aliquot of the glove bag atmosphere into the gas chromatograph. Obtain the chromatogram and measure the oxygen peak area in square centimeters by triangulation. Calculate the partial pressure of oxygen ( $P_{O_2}$ ) in the glove bag according to equation 6 below. Calculate the percentage oxygen by,

$$\% O_2 = \frac{\text{Partial Pressure of Oxygen, } P_{O_2}}{\text{Total Pressure, } P_T} \times 100 \quad (3)$$

$$\text{or } \% O_2 = P_{O_2} \times 100$$

since  $P_T = 1$  atmosphere

When the desired level of oxygen has been reached, seal the vent in the glove bag and reduce the flow of helium into the bag so that it does not balloon and is still flexible. While the flushing operation is being carried out, prepare the dry ice-trichloroethylene trap as a slush. Install under the U-tube cold trap.

#### Analysis of the Gas Phase Above Liquid $N_2O_4$

Attach the 1/4 inch Swagelok nut containing the septum to the 3/8 inch to 1/4 inch reducing union attached to the sidearm of the sample bulb, and screw it down finger-tight. Open the

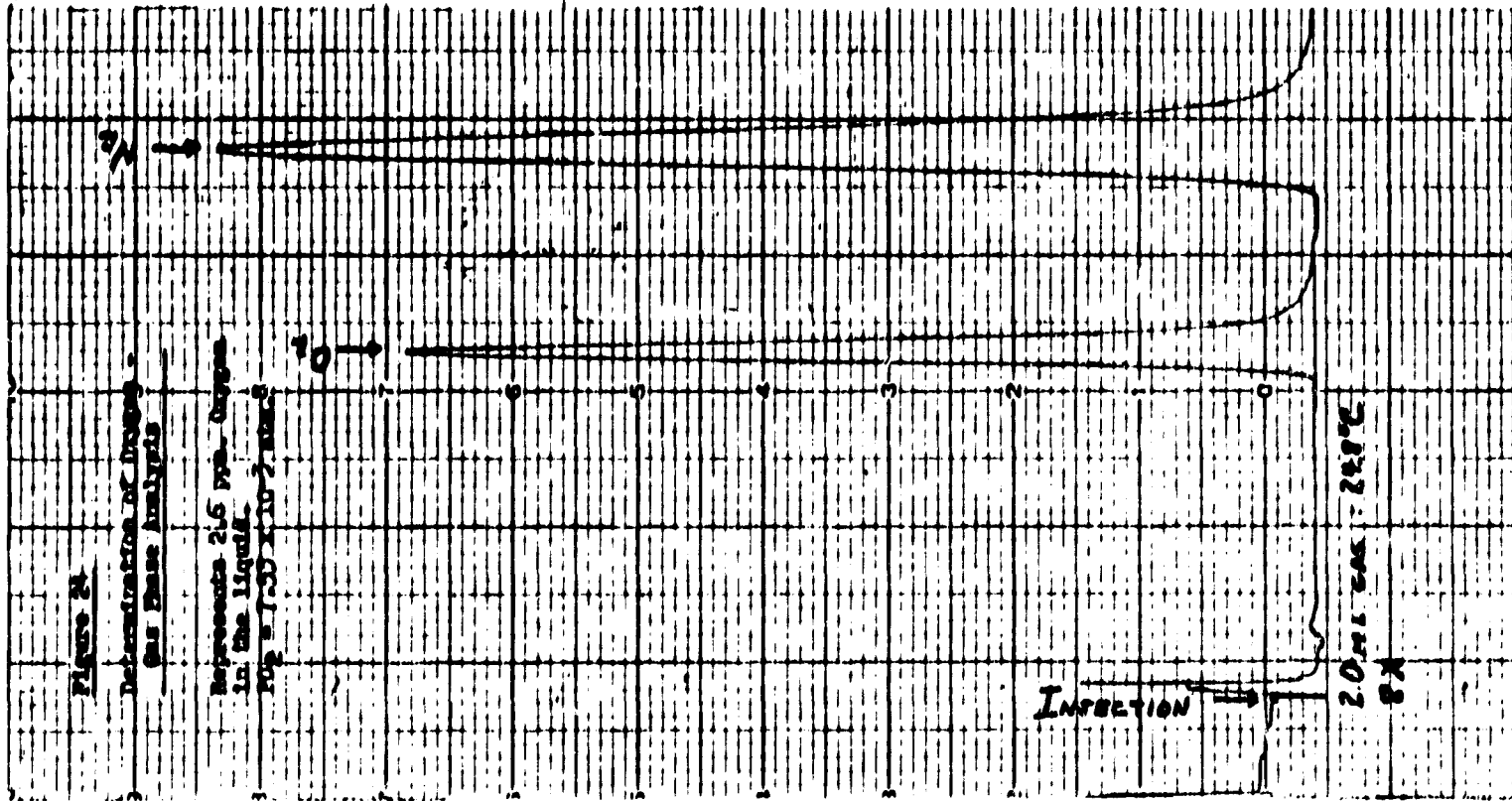


Fisher-Porter valve to the sidearm. Rotate the bulb (invert it) several times to mix the small amount of helium trapped in the sidearm with the gas in the bulb. Be sure that the sidearm has filled up with liquid several times to ensure adequate mixing. Allow the bulb to stand for 15 minutes.

To sample the gas phase, use the Pressure Lok syringe which contains a unique valve in the nosepiece. This valve allows the gas sample in the syringe barrel to be isolated at the same pressure as the gas over the liquid  $\text{N}_2\text{O}_4$ . With the syringe valve open, insert the needle through the septum and withdraw a sample of gas. Avoid holding onto the syringe barrel since enough body heat can be transferred to change the gas composition in the syringe. Close the valve and withdraw the needle from the sample septum. Insert the needle through the inlet septum until it reaches the back of the Swagelok Tee. Open the valve and inject the sample. Remove the needle from the inlet.

Obtain the chromatogram (as Figure 24) and measure the oxygen peak area in square centimeters by triangulation. Calculate the partial pressure of oxygen,  $P_{\text{O}_2}$  in atmospheres, above the liquid  $\text{N}_2\text{O}_4$  from equation 6 below. Calculate the oxygen concentration in the liquid phase in parts per million (ppm.) from  $P_{\text{O}_2}$  and equation 8.

Run five or six replicate gas samples and calculate the average value for the concentration in the liquid phase. The average percent relative standard deviation should be 7 to 8 percent in the range of 2 ppm. to 60 ppm. oxygen.



The cold trap need not be vented after each injection, since the amount of  $N_2O_4$  introduced represents only a few microliters of liquid. Should the trap become plugged, as evidenced by a sharp upward rise of the baseline, proceed as follows:

Turn the three-way valve located after the cold trap (Figure 22, No. 9) to the vent position. Remove the dry ice bath and turn on the Nichrome wire heater. Raise the temperature to about  $150^\circ C$ . and hold there for 5 minutes. Turn off the heater, replace the dry ice bath and allow the trap to cool below  $50^\circ C$ . Return the helium flow to the column. It will be necessary to wait 10 to 15 minutes to allow the air introduced from opening the valve to pass through the column, before another sample is introduced.

#### Analysis of Liquid $N_2O_4$

Insert an aluminum tray into a small plastic bag. Fill the tray with dry ice and insert it under a section of the glove bag. Place a 50 microliter syringe (inside the glove bag) on top of the tray of dry ice (see Figure 23), so that it will be cooled prior to sampling. With the sample arm of the  $N_2O_4$  sample bulb pointed toward the chromatograph, attach the  $1/4$  inch Swagelok nut containing the septum to the  $3/8$  inch to  $1/4$  inch reducing union, and screw it down finger-tight. Open the Fisher-Porter valve to the sidearm.

To sample the liquid phase, rotate the bulb 180 degrees. Insert the syringe needle through the septum into the liquid and slowly withdraw a sample. Do not pull the plunger out too rapidly or there is danger of degassing the sample. Usually there is enough pressure to help force out the syringe plunger so that a minimum amount of pulling is required. Do not hold the syringe barrel tightly as the body heat rapidly warms the syringe causing the sample to be expelled. Remove the needle from the sample and rapidly transfer to and insert the needle in the inlet septum so that it reaches the back of the inlet tee. Inject the sample and remove the needle from the inlet. Expel any  $N_2O_4$  remaining in the needle as it reacts with the epoxy resin used to make the glass-to-metal seal of the syringe.

The capacity of the cold trap is about 140 microliters, so venting will be required every three to four samples. Venting the trapped  $N_2O_4$  is as described for the analysis of the gas phase.

After obtaining the chromatogram (Figure 25), measure the area of the oxygen peak in square centimeters by triangulation. Calculate the concentration of oxygen in the liquid phase in parts per million from equation 9 below.

Run five or six aliquots of the liquid phase and determine the average value for the concentration of oxygen in the liquid phase. The average percent relative standard deviation should be about 10 percent in the range of 2 ppm. to 60 ppm. oxygen.

### Calculations

Calculate the partial pressure of oxygen,  $P_{O_2}$  in atmospheres, from the gas laws by

$$P_{O_2} V = n RT = \frac{g RT}{M} \quad (4)$$

where  $R$  = gas constant = 0.08211-atm./°K-mole

$T$  = absolute temperature, °Kelvin

$g$  = weight of oxygen in grams

$M$  = molecular weight of oxygen = 32

$V$  = volume of the gas space in liters

now

$$g = \frac{F \times A_{O_2} \times 10^{-6} \text{ g./}\mu\text{g} \times V}{V'} \quad (5)$$

where  $F$  = oxygen response factor in micrograms/cm.<sup>2</sup>

$A_{O_2}$  = area of the oxygen peak in cm.<sup>2</sup>

$V'$  = sample or aliquot size in liters

substitution of equation (5) in (4) yields

$$P_{O_2} = \frac{F \times A_{O_2} \times R \times T \times 10^{-6} \text{ (atm.)}}{M \times V'} \quad (6)$$

From the relation (1)

$$X = K \times P_{O_2} \quad (7)$$

where  $X$  = mole fraction of oxygen in the liquid

$K$  = reciprocal Henry's Law constant =  $1.0168 \times 10^{-3}$  at 25°C.

calculate the ppm.  $O_2$  in the liquid from,

$$\begin{aligned} \text{ppm. } O_2 &= 1.0168 \times 10^{-3} \times \frac{32 \text{ g. } O_2/\text{mole } O_2}{92 \text{ g. } N_2O_4/\text{mole } N_2O_4} \times 10 \frac{\mu\text{g.}}{\text{g.}} \times P_{O_2} \\ \text{ppm. } O_2 &= 353.66 \times P_{O_2} \end{aligned} \quad (8)$$

When the liquid is analyzed directly, calculate the concentration of oxygen in the liquid from the relation,

$$\text{ppm. O}_2 = \frac{F \times A_{O_2}}{d_{N_2O_4} \times V'} \quad (9)$$

where  $V'$  is the liquid aliquot size in milliliters and  $d_{N_2O_4}$  is the density of the  $N_2O_4$ , as given by the relation  $d_{N_2O_4} = 1.4916 - 0.00226 (t^\circ\text{C.}) \text{ g./ml. (7).}$

## VI. DETERMINATION OF METALLIC IMPURITIES

### Spectrochemical Analysis

The spectrographic parameters are fully described in the Second Quarterly Report, HRC-67-3, pp. 59-60.

### Atomic Absorption Analysis

The instrumental parameters for the Perkin-Elmer Model 303 Atomic Absorption spectrophotometer used for this work are described in the Second Quarterly Report, HRC-67-3, p. 60. Additional details are outlined in the Perkin-Elmer publication, "Analytical Methods for Atomic Absorption Spectrophotometry".

### Open Dish Evaporation Method of Sample Preparation

The samples of pre-cooled  $N_2O_4$  are transferred from 100 ml. sample flasks into clean tared 200 ml. platinum dishes. After weighing on a Torsion balance, the platinum dishes containing 100-150 grams of  $N_2O_4$  are partially immersed in an ice bath. The  $N_2O_4$  is permitted to slowly volatilize until the volume has been reduced to about 5 ml. Distilled water is then added to the residual 5 ml. and the resultant solution is taken almost to dryness on a low temperature hot plate. Distilled water is used to make up to a final volume of 5 ml. The concentrated solution is analyzed for Fe, Al, Ti and V by atomic absorption analysis, or Fe by Hercules Method M 100-38e.

### Ortho-phenanthroline Iron Analysis - M 100-38e

Iron is reacted with 1,10-ortho-phenanthroline and the resulting color measured. The color complex is stable so that the readings may be taken within a 24-hour period after preparation.

The color development is dependent upon the acidity of the solution. Therefore it is important that the amount of HCl present be the same for the standards and unknown; preferably 1 ml. of 1:1 HCl per 100 ml. of solution.

#### Apparatus

- (1) Spectrophotometer capable of measuring absorbance at 510 m $\mu$ , e.g., Beckman spectrophotometer, Model B.
- (2) Absorption cells, 5 cm. light path.

#### Reagents

(1) 1,10-ortho-phenanthroline solution, 0.1% - Dissolve 0.5 g. of reagent-grade 1,10-ortho-phenanthroline monohydrate (G. Frederick Smith Chemical Company, Columbus, Ohio) in 50 ml. of iron-free ethanol and dilute to 500 ml. with distilled water.

(2) Hydroxylamine hydrochloride solution. - Dissolve 10 g. of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in distilled water and dilute to 100 ml.

(3) Ammonium acetate--acetic acid buffer solution. - Dissolve 100 g. of ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ) in 100 ml. of distilled water. Add 200 ml. of acetic acid, dilute to 1000 ml. with distilled water, and mix. Add one ml. of chloroform as preservative.

(4) Standard iron solution (one ml. = 0.005 mg. Fe). - Dissolve exactly 0.3512 g. of reagent grade ferrous ammonium sulfate, ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ ) in 100 ml. of distilled water and five ml. of conc.  $\text{H}_2\text{SO}_4$ . Dilute with distilled water to one liter in a volumetric flask and mix thoroughly. One ml. of this stock solution will contain 0.05 mg. Fe.



Transfer exactly 100 ml. of this stock solution to a one-liter volumetric flask, add five ml. of 95%  $\text{H}_2\text{SO}_4$ , make up to the mark with distilled water, and mix. One ml. of this solution will contain 0.005 mg. Fe.

Calibration of the Spectrophotometer

Prepare a series of about seven standards as follows in separate 100 ml. volumetric flasks.

<u>Standard</u>	<u>ml. Standard Iron Solution</u>	<u>mg. Iron in Standard</u>
1	0	0.000
2	2	0.010
3	4	0.020
4	6	0.030
5	8	0.040
6	10	0.050
7	12	0.060

Add distilled water to give about 35 ml. total volume, add 1.0 ml. of 1:1 HCl, hydroxylamine hydrochloride solution, etc., finally making up to 100 ml. and mixing as described under Procedure.

Fill a 5 cm. cell with one of the standards and measure the absorbance at 510  $\text{m}\mu$  against the reagent blank. Repeat with the other standards.

Using these absorbance values plot mg. Fe against absorbance to give a calibration curve.

### Procedure

Transfer the sample solution into a 100 ml. volumetric flask. Dilute with distilled water to about 50 ml.

Add 1 ml. of hydroxylamine hydrochloride solution and 10 ml. of 1,10-ortho-phenanthroline solution and swirl to mix. Add 5 ml. of ammonium acetate buffer solution, make up to volume with distilled water, and mix. Allow the solution to stand about 15 minutes.

Run a blank on all reagents in the same manner.

Fill a 5 cm. cell with the solution and measure the absorbance at 510  $m\mu$  against the reagent blank. Refer to the calibration curve, and read the corresponding mg. of iron.

### Calculation

$$\frac{\text{mg. Fe}}{\text{grams of Sample} \times 1000} = \text{ppm. Iron}$$

### Reference

(1) ASTM D 1068

### Closed System Hydrolysis of $N_2O_4$

This method is described in detail in the Second Quarterly Report, HRC-67-3, pp. 64-65.

Briefly, it consists of introducing the sample of  $N_2O_4$  beneath the surface of cold distilled water in a nitration flask, and collecting the off gases in an aqueous  $H_2O_2$  solution. The solutions after concentration can be analyzed by standard atomic absorption methods for the metals of interest or analyzed for iron by the ortho-phenanthroline method perviously described in detail.

### Direct Analysis of Fe by Atomic Absorption Spectrometry

This method is described in detail in the Second Quarterly Report, HRC-67-3, pp. 65-66. Chilled  $N_2O_4$  can be aspirated directly into the spectrophotometer atomizer chamber. The standards used for this analysis are aqueous solutions of iron; therefore, a correction factor must be used in determining the concentration of iron in  $N_2O_4$ .

$$t = \frac{\text{viscosity } N_2O_4}{\text{viscosity } H_2O} \times \frac{\text{density } H_2O}{\text{density } H_2O_4} = \frac{0.4}{1} \times \frac{1}{1.5} = 0.27$$

### $H_2O$ -HCl Hydrolysis of $N_2O_4$

100 ml. of 10% HCl (V/V) is placed in a 500 ml. glass-stoppered, Erlenmeyer flask. The flask is placed in an ice bath and allowed to cool. The sample solution is also placed in an ice bath and allowed to cool. By means of a pipette with a stopcock, a suitable amount (10-20 ml.) of  $N_2O_4$  is then slowly transferred to the flask while the tip is almost touching the bottom of the flask, and is under the surface of the HCl solution. Allow the pipette to drain thoroughly. The flask is then removed from the ice bath, loosely stoppered, and allowed to come to room temperature, while gently swirling. The top must be loose, or constantly lifted to allow escape of the gases. When the  $N_2O_4$  is all absorbed, and the solution is at room temperature, transfer to a 400 ml. beaker and evaporate to a suitable volume, depending on which method will be used for the determination of iron, Atomic Absorption or Ortho-phenanthroline (M 100-38e).

Hercules California Batho-phenanthroline Colorimetric Iron Method

Reagents

(1) Potassium sodium tartrate solution - 10 percent. - Dissolve 10 grams in 100 milliliters of iron-free distilled water.

(2) Hydroxylamine hydrochloride - 10 percent. - Dissolve 10 grams in 100 milliliters of iron-free distilled water.

(3) Sodium hydroxide - 8 N. - Dissolve 320 grams of reagent grade sodium hydroxide in 1000 milliliters of iron-free distilled water.

(4) Batho-phenanthroline - 0.001 M. - Dissolve 0.083 grams in 250 milliliters of ethanol.

(5) Isoamyl alcohol - reagent grade.

(6) Standard iron solution - 0.05 milligrams iron per ml. - Dissolve 50 mg. of reagent-grade iron wire in 25 ml. of reagent grade nitric acid in a 1000-ml. volumetric flask and dilute to 1000 ml. with iron-free distilled water.

(7) Nitric acid - 70 percent ACS reagent grade.

(8) Nitric acid solution - 1 part nitric acid diluted with 4 parts iron-free water.

(9) Hydrochloric acid solution - concentrated, ACS reagent grade, 1 part diluted with 4 parts iron-free water.

Calibration

The calibration curve shall be prepared as follows. Six accurate dilutions from 0.00 to 3.0 micrograms of iron are prepared. These standard solutions along with a blank are transferred to

500-ml. reagent bottles containing 50 ml. distilled water and 5 ml. of concentrated  $\text{HNO}_3$ . Stopper the bottles and mix each solution. To each bottle add 2 ml. of 10% potassium sodium tartrate solution, 10 ml. of 10% hydroxylamine hydrochloride solution and adjust the pH to between 4 and 5 with 8 N sodium hydroxide. Transfer the solutions to 125-ml. separatory funnels and add 5 ml. of batho-phenanthroline solution. Shake to mix and then add 20 ml. of isoamyl alcohol from a buret. Shake well for 30 to 60 seconds. Allow the layers to separate then drain off the alcohol layer through a dry No. 40 Whatman filter paper to remove all water present. Transfer some of the filtrate to a dry 1-cm. path cell and read the absorbance on a spectrophotometer set at 533 millimicrons against a reagent blank for each standard solution. Plot the absorbance as a function of micrograms of iron.

#### Procedure

Weigh a clean 2-ml. glass ampoule to the nearest 0.0002 g. Chill the ampoule in a beaker of crushed ice, then introduce the  $\text{N}_2\text{O}_4$  sample up to the blue line or to about a 2-ml. volume. Freeze the sample, then seal the ampoule with a torch. Allow the ampoule to warm to room temperature, dry, and reweigh to the nearest 0.0002 g. Record the increase in weight as the grams of sample taken. Place the ampoule in a glass-stoppered, 500-ml., heavy-walled iodine flask containing about 50 ml. 1:4  $\text{HCl}$  solution. Stopper the flask, then shake until the ampoule has been broken and all of the  $\text{N}_2\text{O}_4$  absorbed. Filter through a Whatman No. 50 filter paper into a 250-milliliter beaker. Add 2-ml. potassium

sodium tartrate solution, 10 ml. of hydroxylamine hydrochloride solution, then adjust pH to between 4 and 5 with 8 N sodium hydroxide. Transfer to a 125-ml. separatory funnel then add 5 ml. of 0.001 M batho-phenanthroline in ethanol. Shake to mix. Add 20 ml. of isoamyl alcohol from a buret. Shake well for 30 to 60 seconds. Allow the layers to separate then drain off the alcohol layer through a dry No. 40 Whatman filter paper to remove all water that may be present. Catch the filtrate in a dry 1-cm. spectrophotometer cell. Determine the absorbance at 533 millimicrons against a reagent blank. The blank shall be adjusted to pH 4 to 5 with nitric acid solution, and shall contain all of the reagents - including sodium hydroxide - in the same amounts used in conducting the test, except the  $N_2O_4$  sample. Determine the iron content of the sample by reference to a standard curve prepared for this purpose, using reagent-grade iron wire as a standard substance.

Calculation

$$\text{Fe, ppm.} = \frac{\text{Micrograms of Fe found}}{\text{Weight of } N_2O_4 \text{ sample, g.}}$$

Iron Analysis using the Hercules California Hydrolysis and the Rocket Dyne (AFRP-TR-67-227) Extraction Modification of Combined Methods

Preparation of Calibration Curve

Prepare a series of standards by adding 0.0 to 10.0  $\gamma$  standard Fe solution to a 50-ml. beaker. Dilute to 20 ml. with 1:1  $HNO_3$ , add 2 ml.  $H_2SO_4$ , and 2 drops of  $HCl$ . Evaporate slowly to about 5 ml., raise temperature, and evaporate to  $SO_3$  fumes. Cool.

Add 10 ml.  $H_2O$ , 2 ml. 10%  $NH_2OH \cdot HCl$ , and bring to a boil. Cool, adjust the pH to 4 to 5, with 1:1  $NH_4OH$  and 2 M  $NaAc$ . Transfer to a 125-ml. separatory funnel. Add 5 ml. of 0.08% batho-phenanthroline reagent and 10 ml. of isoamyl alcohol. Extract for 10 min. and transfer through dry filter paper to a 25 ml. volumetric flask, discarding the  $H_2O$  layer. Fill to the mark with isoamyl alcohol, mix, let stand for 15 min., and read the absorbance at 533 m $\mu$  against a reagent blank. Plot the absorbance as a junction of  $\gamma$  of iron.

#### Preparation of Samples

The samples are weighed in glass ampoules, and broken under the surface of 50 ml. 1:4  $HCl$ . Allow most of the oxide fumes to be absorbed. When the hydrolysis is complete transfer to a 50 ml. beaker, filling only half full. Add 2 ml.  $H_2SO_4$  and evaporate slowly to about 5 ml. adding the remainder of the sample and washings. Finally evaporate to fumes of  $SO_3$ . Cool. Then proceed as directed in Preparation of Calibration Curve, beginning with - Add 10 ml.  $H_2O$ , 2 ml. 10%  $NH_2OH \cdot HCl$ , etc.

Iron Analysis using the Hercules California Hydrolysis and the Rocket Dyne (AFRP-TR-67-227) Extraction, Second Modification of Combined Methods

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#### Preparation of Sample

The sample is introduced through Teflon tubing directly into glass ampoules which are surrounded by a dry ice-acetone mixture. The  $N_2O_4$  is introduced below the surface of the coolant and frozen immediately. The ampoule is flame sealed, removed from the coolant mixture and allowed to attain room temperature. After weighing the

ampoule is refrozen, and then broken under the surface of 50-ml. ice-cooled 1:4 HCl. Little if any oxide fumes are observed and the  $\text{N}_2\text{O}_4$  is absorbed with a gentle reaction as it melts. The samples are then run according to the procedure as outlined in the preceeding modification of the Combined Methods under Preparation of Calibration Curve, beginning with - Transfer the solution to a 150 ml. beaker and add 2 ml.  $\text{H}_2\text{SO}_4$ , evaporate slowly to about 5 ml., raise temperature and evaporate to fumes of  $\text{SO}_3$ .



## VII DETERMINATION OF COMBINED CHLORINE IN $N_2O_4$ BY X-RAY EMISSION

This method was developed for the determination of traces of combined chlorine in liquid  $N_2O_4$ . It involves hydrolysis of the sample with aqueous  $AgNO_3$ , neutralization of the resulting solution with  $NH_4OH$ , reprecipitation of the  $AgCl$  with  $HNO_3$ , and concentration of the  $AgCl$  by filtration through a Millipore filter. The chlorine content of the precipitate on the filter is specifically determined by x-ray emission using the chlorine  $K\alpha$  line at  $4.73\text{\AA}$ . The limit of detection of the method is  $<1$  ppm. chlorine.

### Apparatus

- (1) X-ray emission spectrometer - General Electric XRD6, or equivalent, equipped with a chromium target tube, a pentaerythritol crystal, and a sample spinner.
- (2) Millipore filtering apparatus consisting of:
  - (a) Pyrex filter holder.
  - (b) Filter flask.
  - (c) Filters - Type GS, 25 mm. diameter and a pore size of  $0.22\mu$ .
- (3) Erlenmeyer flasks, 125 ml., black - prepared by spraying the outside of the flasks with black paint, but leaving a spot on the bottom (ca. 1-inch diameter) free of paint which is used to observe indicator color changes.
- (4) Beaker, 50 ml., black. Spray outside of beaker with black paint.

### Reagents

- (1) Distilled water - chloride free.
- (2) Nitric acid - 1:1 by volume.
- (3) Silver nitrate - 5% aqueous solution.
- (4) Ammonium hydroxide - 1:1 by volume.
- (5) Potassium chloride - Analytical reagent grade,  
dried for 1 hour at 105°C. and stored in a dessicator.
- (6) Isopropanol - Chloride free analytical reagent grade  
filtered through 22 Millipore if necessary to remove  
any particulate matter.
- (7) Chloride stock solution - Accurately weigh 0.210 g.  
of dried KCl into a 1-liter volumetric flask.  
Dissolve in chloride-free distilled water, dilute  
to volume, and mix thoroughly.
- (8) Chloride standard solution, 10µg. Cl/ml. -  
Accurately pipet 25 ml. of the above stock solution  
into a 250-ml. volumetric flask. Dilute to volume  
with chloride-free distilled water and mix thoroughly.

### Calibration

Prepare a series of standards by pipetting 1, 2, 3, 4, 5 and 6 ml. of the chloride standard solution into black, 125-ml. Erlenmeyer flasks. To each flask add 5 ml. of 5% AgNO<sub>3</sub> and 3 ml. 1:1 HNO<sub>3</sub>. Neutralize the solution with 1:1 NH<sub>4</sub>OH using phenolphthalein indicator. Acidify with 1 ml. of 1:1 HNO<sub>3</sub>, allow to stand 5 minutes, then cool to 0°C. in an ice bath. Assemble the Millipore filter assembly and quantitatively filter the

contents of the flask using vacuum. Suck the filter dry, then wash with two 10-ml. portions of cold distilled water acidified with 1 drop of concentrated  $\text{HNO}_3$ . Rinse the sides of the filter holder with 2 ml. of chilled isopropanol to wash down any  $\text{AgCl}$  adhering to the filter holder. Carefully remove the filter from the filter holder (avoid skin contact), cover with a black, 50-ml. beaker, and allow to air dry. Mount the dried filter as shown in Figure 26 and place in the sample spinner. Measure the total counts at the  $2\theta$  and background angles using the following instrumental parameters.

Path - helium

Counting time - 100 sec.

Target - chromium

X-ray power - 37 ma, 55 KV at constant potential

Crystal - pentaerythritol

$2\theta$  angle -  $65.49^\circ$

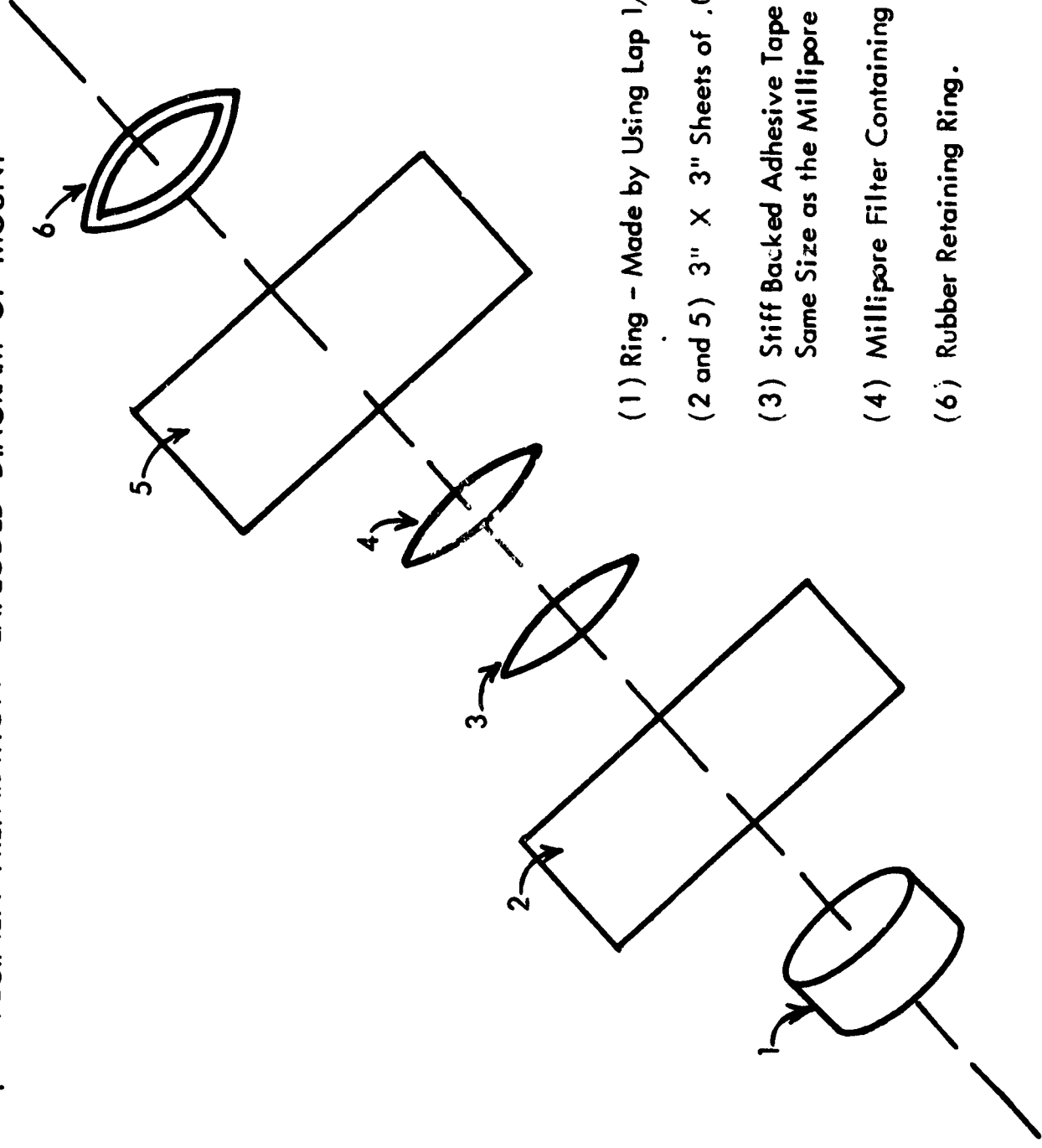
Background angle -  $67.49^\circ$

From the net counts ( $2\theta$  - background), calculate the intensity ratio of each standard relative to the most concentrated standard. Plot intensity ratio versus  $\mu\text{g. chlorine}$ .

#### Procedure

A sample size should be selected to contain 20-50 g. of chlorine (usually ca. 5 ml.). Introduce a portion of the sample into a 125-ml. Erlenmeyer flask and chill to  $0^\circ\text{C}$ . in an ice bath. Pipet 5 ml. of 5%  $\text{AgNO}_3$  into a 50-ml. Erlenmeyer flask and cool to  $0^\circ\text{C}$ . Using a chilled pipet, slowly add the cold

X-RAY SPECIMEN PREPARATION - EXPLODED DIAGRAM OF MOUNT



sample to the flask without mixing. Place the flask in the ice bath and allow to remain undisturbed until the two layers become one. Remove from the ice bath and allow to warm to room temperature. Direct a slow stream of nitrogen into the flask and swirl until the majority of the brown fumes are gone. Complete removal of the brown fumes by warming on a steam bath.

Quantitatively transfer the contents of the flask to a black, 125-ml. Erlenmeyer flask with the aid of a little chloride-free distilled water. Neutralize to phenolphthalein with 1:1  $\text{NH}_4\text{OH}$  and proceed as described under Calibration. Carry a chloride standard of the same concentration as the calibration reference standard through the entire procedure at the same time. From the net counts of sample and standard, calculate the intensity ratio. Read the micrograms of chlorine present in the sample from the calibration curve.

Calculation

$$\frac{\text{micrograms chlorine}}{\text{ml. sample} \times 1.49} = \text{ppm. combined chlorine}$$

$$\text{ppm. Cl} \times 1.85 = \text{ppm. NOCl}$$

The relative standard deviation of results in the recommended concentration range should be 2-4%.